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SULFUR AND NITROGEN BALANCES IN THE SOLVENT REFINED COAL PROCESS

Charles H. Wright

Pittsburgh and Midway Coal Mining Company

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January 1975

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SULFUR AND NITROGEN BALANCES IN THE SOLVENT REFINED COAL PROCESS

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The report gives results of an exact elemental balance study of the Solvent Refined Coal (SRC) process that was conducted with the laboratory reactor to determine the fate of sulfur and nitrogen in the SRC process. The work was performed in late 1972 as part of a normal experiment with Kentucky No. 9 high volatile B bituminous coal and a blend of processed anthracene oils under 1000 psig hydrogen pressure. A variety of technique studies had been made in preparation, such as investigation of the effects of sample size on analysis and methods of handling all samples of input and output material for maximum recovery and representative composition. Accounting for carbon and hydrogen was accurate, for sulfur good, and for nitrogen poor. A detailed comparison of conventional Kjeldahl and Dumas analytical results for nitrogen in coal and solid products revealed that input nitrogen is not fully reported by Kjeldahl and that sample size affects nitrogen results reported by Dumas. Nitrogen analysis needs further investigation. The study forced review of sampling and handling techniques as well, with salutary results in laboratory work.

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ABSTRACT

The purpose of an exact elemental balance study of the solvent Refined Coal (SRC) process with the laboratory reactor was to determine the fate of sulfur and nitrogen fed in the slurry. The work was performed in late 1972 as part of a normal experiment with Kentucky #9 high volatile B bituminous coal and a blend of processed anthracene oils under 1000 psig hydrogen pressure. A variety of technique studies had been made in preparation, such as investigation of the effects of sample size on analysis and methods of handling all samples of input and output material for maximum recovery and representative composition. Accounting for carbon and hydrogen was accurate, for sulfur good, for nitrogen poor. A detailed comparison of conventional Kjeldahl and Dumas analytical results for nitrogen in coal and solid products revealed that input nitrogen is not fully reported by Kjeldahl and that sample size affects nitrogen results reported by Dumas. Nitrogen analysis needs further investigation. The study forced review of sampling and handling techniques as well, with salutary results in laboratory work. For similar balance study in any scaled up version of the upflow reactor, a preliminary attempt for the purpose of discovery and procedure development should precede the final detailed work.

This report was submitted in partial fulfillment of Agreement Number EPA-IAG-D4-0454 between the U. S. Enviromental Protection Agency and the office of Coal Research, U. S. Department of the Interior. Work was performed by the Pittsburg & Midway Coal Mining Company under Office of Coal Research contract 14-01-0001-496 and was completed during October 1974.

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SECTION I
CONCLUSIONS

The elemental balance study revealed shortcomings in the handling of feed coal, a need for better suspension of mineral matter in feed slurry, a need for larger samples for analysis, a need for changes in sampling techniques, and a need for a better analytical method for nitrogen in feed coal and SRC products.

Material recovery, 98% at the time of the study, is currently 99% or better as a result of subsequent improvements. This is significant because reactor behavior permits a preferential segregation of mineral, which is rich in sulfur; laboratory-size, short-interval samples reveal variations in ash content, forcing a prorating of lost sulfur to the product distribution. The loss of water from the slurry feed vessel has similarly been controlled.

The balances for carbon and hydrogen are accurate, for sulfur good. Accounting for nitrogen from raw data is awkward because output exceeds input, especially by conventional Kjeldahl analyses; the effect of sample size on Dumas analysis of feed coal is demonstrable, and other analytical methods for products have special limitations.

It is clear that the SRC process removes from coal nearly all of the ash, most of the sulfur, and less of the nitrogen. To remove an appreciable fraction of the nitrogen might require liquefaction under conditions that convert all material to hydrocarbons of appreciably lower weight than is usual now in the SRC process.

SECTION II
RECOMMENDATIONS

Insofar as they would apply to the laboratory reactor operation, many of the recommendations arising from the study have already been adopted:

1. The uniformity of feed coal composition was achieved by adopting the ASTM long pile sampling method for handling initial lots, by improved methods for homogenizing the ground sublots, and other procedures.
2. The uniformity of feed slurry has been greatly improved by modified grinding and sieving equipment for the coal, modified stirring of slurry in the feed vessel for suspension of mineral, and by avoidance of the need to warm slurry and hence lose contained water from the input.
3. The effect of holdup of material in sample flasks has been significantly reduced by taking larger samples and, when appropriate, leaving flasks uncleaned for a relatively constant holdup of mineral-rich material between runs; so that raw material recovery is good, mass balances are regularly closed above 99%, and exact elemental balances are facilitated.

For exact nitrogen balances, analytical methods other than Kjeldahl and Dumas should be investigated. This is particularly true for feed coal, solids, and high molecular weight products.

In any scaled up operation of the SRC process, an exact element-by-element balance will require good understanding of mineral behavior in the dissolver and its operating characteristics. Recovery of either 100% raw material or 100% ash is unlikely. Therefore, a preliminary elemental balance study should be undertaken for the purpose of discovery and procedure development some months before final detailed study of scaled up SRC process operation.

SECTION III
INTRODUCTION

III-A SCOPE OF THIS REPORT

Section I presents conclusions reached from the detailed elemental balance studies of the SRC process reported in Section V.

Section II lists those recommendations, chiefly affecting handling and workup of samples and certain analytical methods, resulting from the studies.

This section sketches the background for this report and the general objectives of the continuous reactor program in the SRC process.

Section IV describes the laboratory reactor in use when the studies were made. It includes typical operating procedure, typical workup of the coal solution samples, and typical analytical methods then employed.

Section V describes experiment CU 48: its objectives, the materials used, run conditions, yields, product distribution and compositions, and the elemental balances.

Section VI evaluates the errors, problems, and gains of the study.

The glossary contains all special terms and abbreviations used in this report. The appendices include certain detailed analytical methods employed, worksheets, illustrations of infrared spectra for various solvents, and similar supporting data.

III-B BACKGROUND

Studies in the 1960's related to the solvent refining of coal had been conducted in a laboratory batch autoclave and in a continuous unit capable of processing about 23 kilograms (50 pounds) of coal per hour. In these experiments the material balances had generally been closed to account for most (often 98-100%) of the materials fed to the reactor. However, the balance made for each individual element had been made with variable accuracy. Some suggestion of the range of reported values is found in OCR R&D Report No. 9 (Gulf Oil):

	GRAMS IN	GRAMS OUT	
		Run B-55	Run B-62
C	505.4	503.0	519.9
H	35.16	28.6	35.03
N	4.96	5.29	6.52
S	9.48	6.69	5.43
O	20.98	13.58	20.49
Ash	15.50	14.9	11.14

As a rule the balances for carbon were closed accurately, and for hydrogen reasonably well; but sulfur was lost from the system, and the products failed to account for the amount of sulfur fed.

Another problem was that nitrogen obtained from the products frequently exceeded nitrogen reported in materials fed into the reactor, in the examples given above, by 0.3 to 1.6 g.

The problem with nitrogen was also evident in work done with other coal conversion processes. OCR R&D Report No. 39 (Consolidated Coal) reported three elemental balances:

	1356-1		1356-2		1356-3	
	GRAMS		GRAMS		GRAMS	
	IN	OUT	IN	OUT	IN	OUT
C	621.29	620.98	619.92	621.74	625.02	627.66
H	52.71	52.19	53.34	53.06	54.19	54.24
N	3.81	3.82	4.31	4.22	4.87	5.38
O	22.09	22.68	23.24	21.98	25.56	24.53
Organic S	8.42	7.20	7.85	5.55	6.59	5.15
Inorganic S	6.99	6.91	7.00	7.60	7.04	7.03
Ash less inorganic S	26.60	28.14	26.64	27.98	26.78	29.55

These balances were obtained from a much milder reduction process than the other two, and presumably output would look more like input. One of Consolidated's three balances and all P&M* balances show more nitrogen in products than in feed.

Such results indicated sampling errors and probably some inaccurate analytical methods. The Environmental Protection Agency (EPA) had received coal process data from reports by Pittsburg & Midway Coal Mining Co. (P&M) and others; the EPA was interested in obtaining more accurate results than those currently available. The best laboratory data from the P&M Process Development Plant or laboratory tended to close the elemental balance for carbon most of the time, for hydrogen some of the time, for sulfur and nitrogen not usually. P&M was therefore asked to make studies of the technique, sampling, and analytical methods necessary to close these balances.

This work required, first, that the continuous laboratory reactor be operated by the best method for making samples, and, second, that these samples be the basis for analytical studies designed to develop a closed elemental material balance. The problems attacked fell into several categories:

*The Pittsburg & Midway Coal Mining Company, a subsidiary of Gulf Oil Corporation.

Materials preparation and analysis

Reactor operating techniques designed to obtain well controlled and well validated samples

Sampling and workup techniques which should produce a set of samples capable of producing an elemental balance

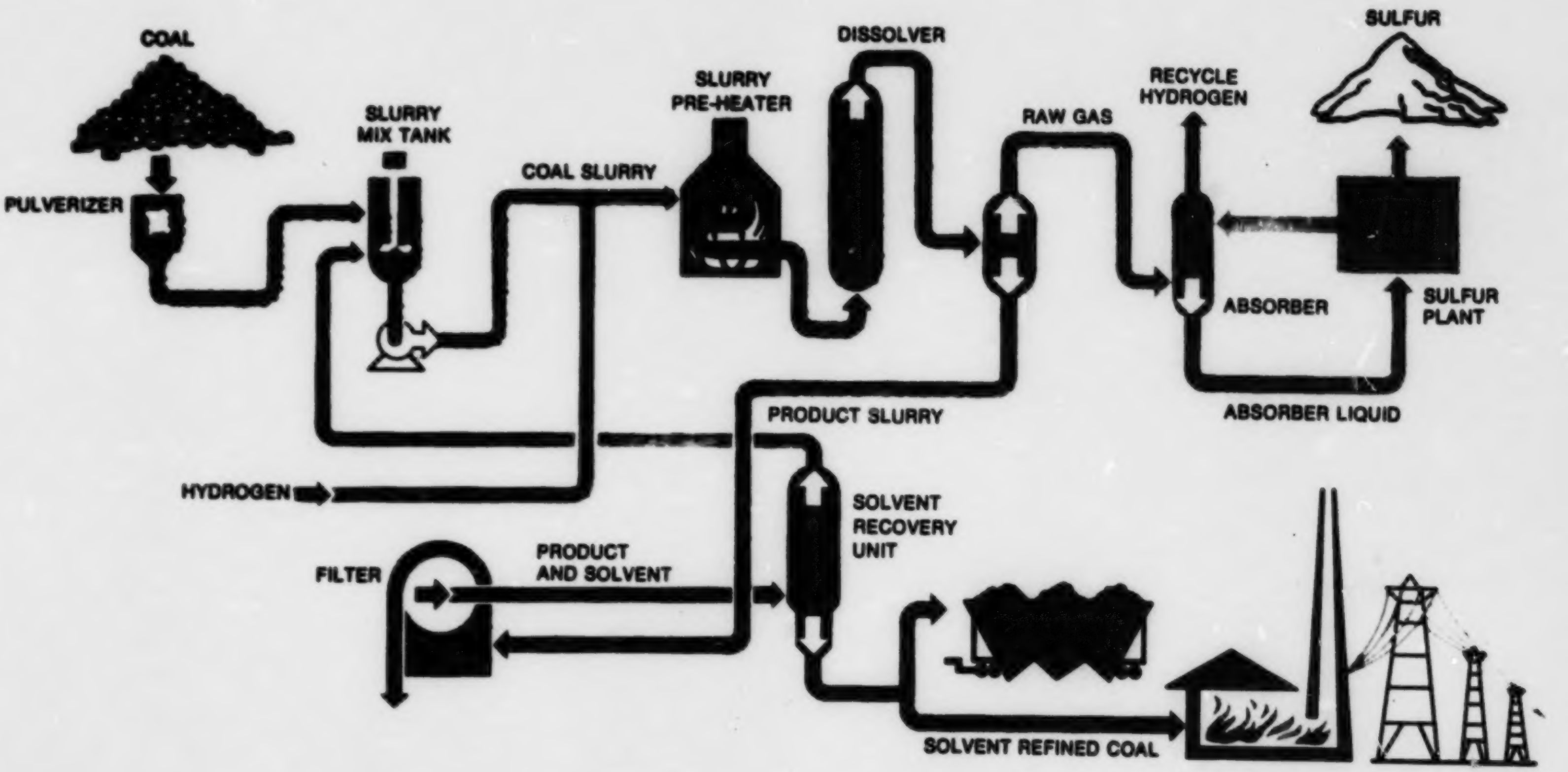
Analytical methods which produce accurate results

Eventually these balances will have to be repeated in the Tacoma (Fort Lewis) Pilot Plant studies. The number of vessels involved, and therefore the number of accurate samples needed, will probably be larger. This in turn will probably require a considerable study of sampling before accurate material balances are obtained. From such samples the element-by-element balance should be possible. In addition to studies with the major elements, the Pilot Plant will eventually conduct a sampling campaign to produce balances for a number of trace elements which affect the environment. The laboratory studies reported here are thus the leading effort in a more extensive work plan.

III-C GENERAL OBJECTIVES OF THE CONTINUOUS REACTOR PROGRAM

The goal of all processes to upgrade coal is to produce a fuel high in Btu/lb and low in sulfur and ash. In the Solvent Refined Coal process (figure 1), coal is dissolved without added catalyst under moderate hydrogen pressure in a solvent generated by the process itself. Most organic matter in the feed coal dissolves. The liquid can be filtered to remove mineral matter and unreacted carbonaceous matter, and the filtrate can be subjected to vacuum flash distillation for solvent recovery. The vacuum flash residue is the upgraded coal. Some light hydrocarbon byproducts are obtained also.

SOLVENT REFINED COAL PROCESS


COAL
PULVERIZER
SLURRY MIX TANK
COAL SLURRY
HYDROGEN
SLURRY PRE-HEATER
DISSOLVER
RAW GAS
RECYCLE HYDROGEN
ABSORBER
ABSORBER LIQUID
SULFUR
SULFUR PLANT
PRODUCT SLURRY
FILTER
PRODUCT AND SOLVENT
SOLVENT RECOVERY UNIT
SOLVENT REFINED COAL

Richards Studio, Tacoma

Figure 1 SRC Process, Simplified Schematic

The general objective of the autoclave program (OCR Interim Report No. 6, Vol. II, Part 1), to improve our knowledge of the chemistry of the coal solution process, is the same in the continuous reactor program. During the 1970's the parts of this study have included:

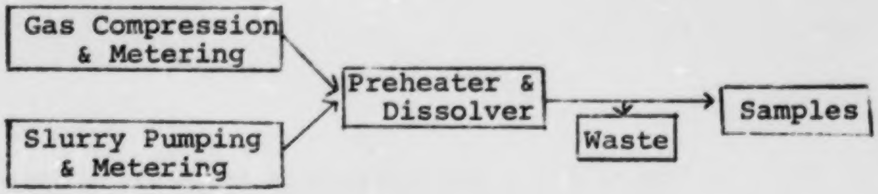
1. Investigation of a reactive initial solvent for startup
2. The modeling of startup conditions at the Tacoma Pilot Plant
3. The development of suitable sampling techniques, handling methods, and accurate analytical methods which collectively should monitor the reaction, account for materials fed in, and permit valid correlations of results from run to run
4. Establishment of operating conditions for a given solvent and coal at a given ratio which produce or reproduce enough reusable solvent and other desired products
5. Investigation of carbon monoxide and hydrogen as reducing gas and the effects of shift reactions in the reactor
6. Examination of the effects of catalysts, different reducing gases, different retention times in the reactor, and similar variables

SECTION IV
EQUIPMENT AND PROCEDURES

This section discusses the continuous reactor, the operating procedure, typical workup of process materials, and methods of analysis employed at the time experiment CU 48 was done. An understanding of the process and analytical techniques is prerequisite to evaluation of results obtained, and to assessment of probable results to be expected from a large scale reactor.

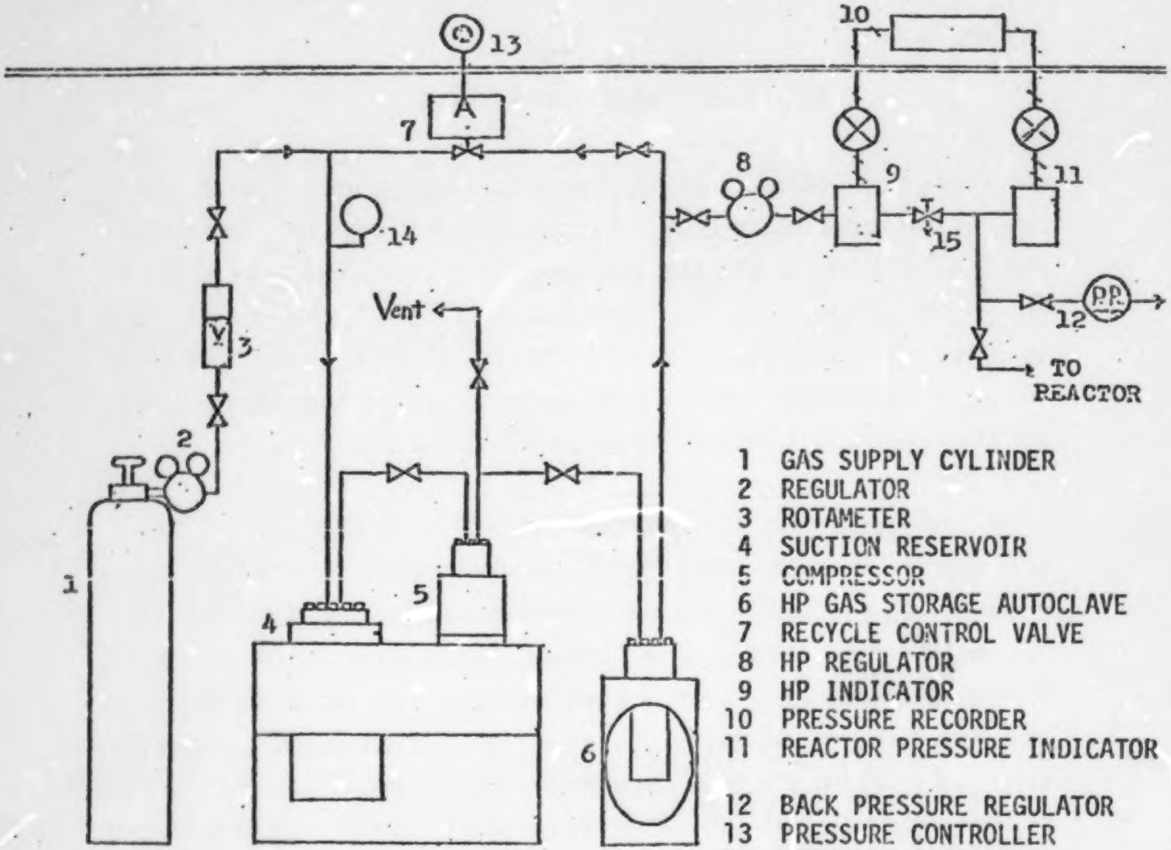
IV-A DESCRIPTION OF THE CONTINUOUS REACTOR

The continuous reactor may be considered as several interconnected systems. These systems, repeatedly modified since CU 48 to model the Tacoma Pilot Plant design or to improve operation, are described as they existed during the experiment reported. (Further information is available in Office of Coal Research R&D Report No. 53, Interim Report Nos. 7 and 8.) The following block diagram shows the relationship; when samples are not being taken, the flow through the reactor is directed to the waste receiver and gas is vented.



IV-A-1 Gas Compression and Metering System

This system (figure 2) is designed to take hydrogen from a standard gas storage bottle, compress and store a reserve of this gas above reactor operating pressure, and then meter the stored gas into the reactor. The system provides for calibration of gas delivery at operating


13
10
A
7
8
9
11
15
14
Vent
3
2
P.R.
12
TO REACTOR
1
4
5
6

1	GAS SUPPLY CYLINDER
2	REGULATOR
3	ROTAMETER
4	SUCTION RESERVOIR
5	COMPRESSOR
6	HP GAS STORAGE AUTOCLAVE
7	RECYCLE CONTROL VALVE
8	HP REGULATOR
9	HP INDICATOR
10	PRESSURE RECORDER
11	REACTOR PRESSURE INDICATOR
12	BACK PRESSURE REGULATOR
13	PRESSURE CONTROLLER
14	PRESSURE INDICATOR
15	NEEDLE METERING VALVE

Figure 2 Gas Compression and Metering System

pressure, and for recording both delivery pressure and operating pressure in the reactor. Hydrogen flow is adjusted by maintaining a controlled differential pressure across a metering valve.

In figure 2, commercial size 1A gas cylinders deliver gas through a high pressure (HP) regulator and HP rotameter to the suction end of the compressor. The rotameter, Brooks 1410-01D1B1A, is operable to 134 kg/cm^2 (1900 psig) at 37.7°C (100°F). Since the compressor, Aminco 46-4025SP, operates with a suction in the 56-70 kg/cm^2 (800-1000 psig) range, gas cannot be completely pumped from a cylinder with this compressor. The suction reservoir for this compressor is an autoclave vessel, Autoclave Engineers 3-3/4-liter (1-gallon) size. It maintains gas at regulated input pressure, normally 56-70 kg/cm^2 (800-1000 psig), set by the regulator on the gas cylinder. The air-operated compressor takes gas from the suction reservoir, boosts its pressure, and stores it in a 1-liter HP gas storage autoclave at 155-190 kg/cm^2 (2200-2700 psig). Gas from this storage autoclave passes through an HP regulator and needle metering valve to the reactor. Excess compressed hydrogen is recycled to the suction side of the compressor through a pneumatic recycle control valve, Annin 5060, whose setting thereby controls the pressure maintained in the HP storage autoclave.

The flow of gas to the reactor is metered by the needle valve; high side and low side regulators govern the flow. High side pressure to this valve is set on an HP regulator, Marotta RH-292GA-35-2222, located between HP storage autoclave and needle valve.

Low side pressure is set by the reactor operating pressure, maintained as described later. The HP needle metering valve, though adjustable if necessary upon changing types of reducing gas, in practice is seldom readjusted. A pressure recorder, Foxboro Consitrol 5420 F-E, provides a continuous record of pressures on each side of the metering valve. The recorder operates through differential pressure cells, Foxboro 11 GM Force Balance Pneumatic Pressure Transmitter units. Bourdon type indicating gages provide separate checks on recorder performance.

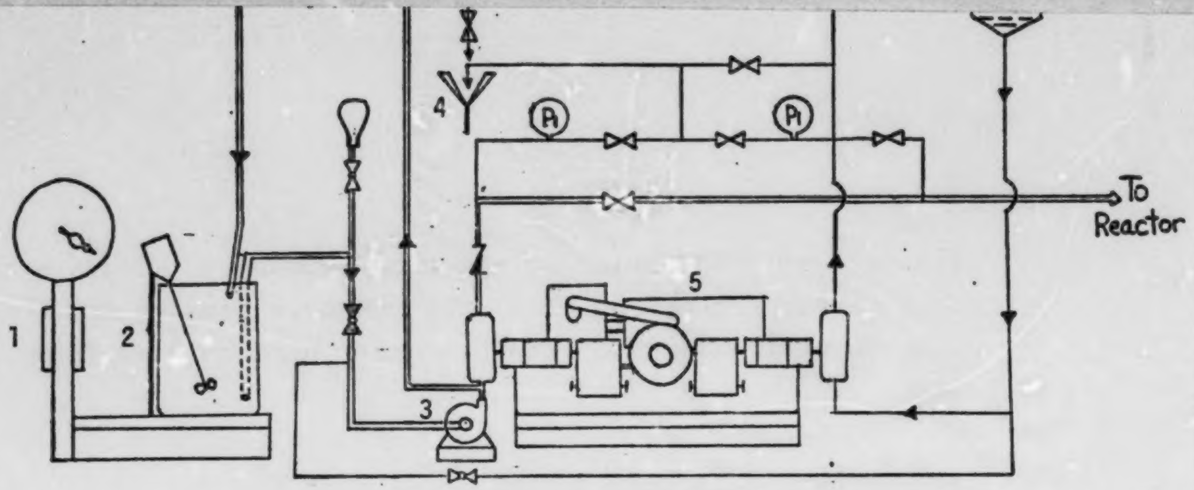
To calibrate flow through the HP needle metering valve, gas to the reactor is diverted through a Grove Model S-91XW back pressure regulator, set at the desired reactor operating pressure, to an exit line. Differential pressure between the HP regulator and the back pressure regulator determines gas out; the volume is measured by a wet test meter at the exit line. Minor volume adjustments per unit time are controlled by small changes in differential pressure, and larger adjustments are made by resetting the needle valve also. Initial calibration of hydrogen flow to desired reactor delivery rate therefore requires both a valve setting and an operating differential pressure to be established which will result in desired flow at desired pressure. Any subsequent calibration is then accomplished by minor adjustments of the differential pressure. (The back pressure regulator is adjusted by setting a gas pressure in the head of a pressure dome.) Nitrogen lines, not shown in figure 2, are provided to pressurize the back pressure regulator for readjustment when necessary and to purge reducing gas from the reactor or gas compression system when necessary. Air supply lines for operation of the pressure sensing and pressure controlling devices have also been omitted from figure 2.

IV-A-2 Slurry Pumping and Metering System

This system (figure 3) maintains a uniform slurry, pumps it into the reactor at a uniform rate, and measures the pumping rate accurately. In addition, it maintains a supply of solvent for startup and shutdown.

Reliable performance of this system is essential to satisfactory reactor operation. Failure of a pump in this system is the most common cause of subsequent difficulty in the other systems. When flow is stopped in the preheater or dissolver, repolymerization or even coke formation in the high temperature vessels commonly results. Either condition may permanently plug the preheater.

Coal and solvent in weighed amounts are mixed separately and then transferred to the slurry feed vessel (figure 3), a stainless steel vessel of about 8 liters capacity. It is fitted with a stirrer, operated continuously to keep the coal suspended in the solvent. Slurry is drawn up through a dip tube reaching close to the bottom of the feed vessel, an arrangement allowing room for the scale to move and so permit weighing of the feed vessel, and circulated (during CU 48) by a centrifugal pump. The dip tube is stainless steel, rigid enough to stand securely in place when connected to the feed line for the centrifugal pump. The return stream of slurry was made to run down the dip tube to reduce a tendency to inject air


4
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5
1
2
3

Figure 3 Slurry Pumping and Metering System

bubbles below the surface of slurry in the feed vessel.

Slurry in the recirculating loop provides feed for the suction of the dual head feed pump, Hills McCanna UM2F. One pump head is used only for standby and only to pump flush oil when necessary. The other standard pump head was replaced because its internal volume was too large for pumping slow feed rates of coal slurry and because coal settled out in the pump head. The replacement pump head, Autoclave Engineers Speed Ranger, catalog No. 10-4440, was more suitable.

The slurry pumping and metering system thus contains two feed vessels, one for coal slurry and one for flush oil. Piping allows the pumping of flush oil by either pump head, but coal slurry only with the modified pump head. By this design, solids may be flushed from the slurry head when necessary. In normal operations the reactor is started up with flush oil pumped by the Autoclave Engineers pump head, which is primed by the centrifugal pump circulating flush oil. Before the experiment, the operator cuts off the flow of flush oil and substitutes feed slurry. The auxiliary pump head is normally kept working against a back pressure regulator in order to keep the pump ready for rapid switching from the pump head feeding slurry to the other feeding only flush oil.

IV-A-3 Reaction and Sampling Systems

The reactor has two functions: to dissolve coal, and then to further hydrogenate the initial reaction products. During initial heating of the coal-solvent slurry, most of the coal is dissolved by a hydrogen transfer reaction which is largely completed in the preheater. The solution is then kept hot and in contact with hydrogen for some time to hydrogenate the initial reaction product. Figure 4 is a configuration diagram of the reactor.

The preheater is a coil of high pressure tubing in a fluidized sand bath. The dissolver is a 450-ml autoclave vessel designed for upflow of material. The designs permit operating these vessels at different temperatures, and thus match the capability of the pilot plant for the SRC process.

The preheater tube used during CU 48 was a 5.4-meter (18-foot) length of 0.278-cm (7/64-inch) ID pressure tubing with a volume of about 33 ml; the combined volume of the preheater and dissolver, with allowance for all void space and the volume of the thermowell, was estimated to be 485 ml. For this volume of reactor space, and with a nominal slurry density of 1.15 g/ml, a feed rate of 450 ml/hr of cold slurry corresponds to a liquid hourly space velocity (LHSV) of about 1 through preheater and dissolver. Experiments have been reported with retention time referred to the dissolver (LHSV of 1.0 = 520 g/hr in most reporting done). The LHSV values are omitted in this report for the following reasons. The relative volumes of the gaseous and liquid phases actually present in the reactor are difficult to estimate with precision: the liquid expands when it is heated; gas bubbles from injected hydrogen displace the liquid; and, further, the solution absorbs reducing gas, reacts with it, and forms various gaseous products. The "true retention time" is therefore less than the reciprocal of LHSV by the factor which relates the relative volume of gaseous and liquid phases.

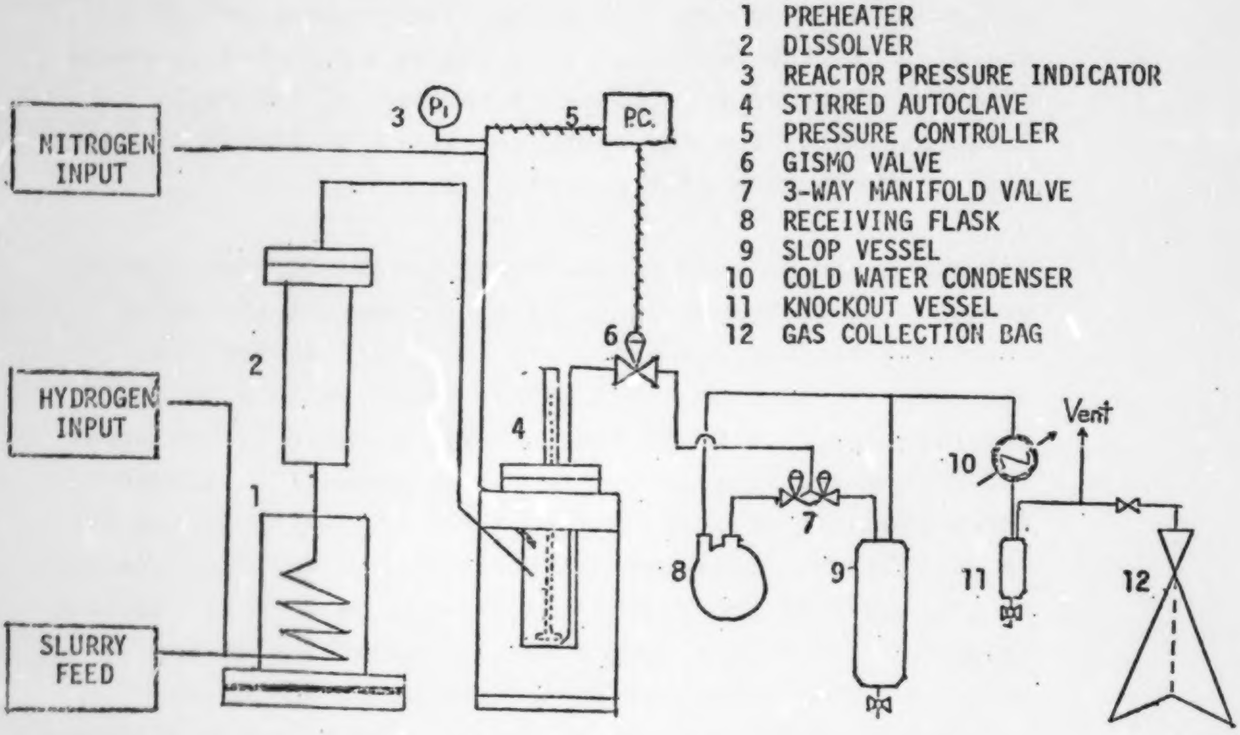

1 PREHEATER
2 DISSOLVER
3 REACTOR PRESSURE INDICATOR
4 STIRRED AUTOCLAVE
5 PRESSURE CONTROLLER
6 GISMO VALVE
7 3-WAY MANIFOLD VALVE
8 RECEIVING FLASK
9 SLOP VESSEL
10 COLD WATER CONDENSER
11 KNOCKOUT VESSEL
12 GAS COLLECTION BAG
NITROGEN INPUT
HYDROGEN INPUT
SLURRY FEED
P_1
P.C.
Vent
1
2
3
4
5
6
7
8
9
10
11
12

Figure 4 Reaction and Sampling Systems

The temperature of the preheater sand bath is measured by means of thermocouples in the sand and between heaters and outer wall of the sand bath. The temperature of the fluid in the preheater coil can be estimated by means of a thermocouple in a block at the top of the coil. Effluent fluid from the preheater flows through a transfer line to the bottom of the dissolver.

The dissolver is a stainless steel bolted-closure pressure vessel. It is cylindrical, with an internal volume of about 450 ml, approximately 3.8 cm (1-1/2 inches) in diameter and 38.5 cm (15.1 inches deep), with a hemispherical end 4.4 cm (1-3/4 inches) in radius. The upper end of the cylinder is 4.4 cm (1-3/4 inches) in diameter for a distance of 1.72 cm (1/2-inch), tapering to the 3.8 cm (1-1/2-inch) diameter. A thermocouple well is attached to the cover of the vessel and extends 30.5 cm (12 inches) below the cover into the cavity. Connections at the bottom of the vessel and in the center of the cover accomodate standard cone and thread high pressure fittings. In addition, a hole is drilled through the body of the vessel near the top for attachment of a rupture disc assembly. The enlarged hole near the top is within the flange provided for the bolted closure. The vessel OD is 6.3 cm (2-9/16 inches), which results in a wall thickness of 1.33 cm (17/32 inches) over most of the length. The dissolver is heated by means of electrical heaters wound around the outside, covered by insulation.

Liquid product is taken from the top of the dissolver vessel through an electrically heated transfer line to a 2-liter stirred autoclave. Product is removed continuously through a dip tube reaching the bottom of the autoclave. The main function of the autoclave is to provide a surge capacity to smooth out pressure fluctuations. Product is removed from the system by allowing gas and liquid to flow out through a Fisher Governor "Gismo" control valve. This valve is air-operated; it balances the operating pressure in the reactor against a bellows containing a controlled air pressure. The bellows moves the valve stem in and out to open or close the orifice in the pressure letdown valve. All product made must flow through this orifice. Both valve stem and orifice in this valve are tungsten carbide, which precludes rapid wear from ash minerals flowing through the pressure letdown orifice. The sample flows from the pressure control valve and is directed to the collection flask through an air-operated three-way valve or, if a sample is not being collected, into a slop receiver instead. Samples are collected in 3-liter stainless steel flasks with suitable standard taper joints. These are connected in the system by means of stainless steel standard taper fittings; sample flasks have two necks, each with a 29/42 standard taper joint. These joints are sealed with vacuum grease and secured by clamps tightened with thumbscrews to prevent pressure surges causing joints to leak. Gas flows out of the flask through a water cooled condenser. Condensate is collected in the knockout vessel. Gas is collected in a rubberized fabric gas collection bag or vented, as desired. Generally it is necessary to collect liquid and gas samples for different lengths of time to permit the air to be flushed out of the flask. The gas sample is taken for a timed interval near the end of the liquid sampling period.

To prevent materials from contaminating pressure gages and the pressure control tap of the Gismo valve, the lines from the reactor to the gages are flushed with nitrogen. Nitrogen is pumped into the system by means of a Ruska pump, model 2284, at a constant rate and delivered to the top of the 2-liter autoclave used as surge vessel. Thus, pressure for the reactor is measured at this point, by measuring pressure in the nitrogen purge line which is at system pressure. This pressure is controlled by the setting of the "Gismo" control valve.

In the usual mode of operation the "Gismo" valve is set at desired system pressure, and all liquid and gas from the autoclave goes from the pressure of the reaction system to atmospheric pressure as the sample flows through this valve. Both liquid and gas flow down and enter either the slop vessel or the sample collection flask, depending on the setting of the air-operated valve. The slop vessel, an alternative receiver, is used whenever a normal product is not being collected, as when collection flasks are being changed, to receive lineout materials or off-specification materials, etc. Gas is disengaged from the liquid and flows from the flask through a condenser to a vent or to a gas sampling bag as required. Gas is also disengaged from the liquid in the slop receiver, and this normally flows to the vent.

As liquid and gas flow from dissolver to autoclave, liquid which accumulates will normally be removed from this vessel through the dip tube which reaches to the bottom of the autoclave. The retention of liquid in this vessel is therefore limited to the time required for liquid to drain to the bottom and be collected by the dip tube. This vessel is operated at a temperature well below reaction temperature and so does not contribute reaction time. The nitrogen from the gage purge also enters this vessel, and the gas sample therefore contains a fraction of nitrogen which is metered into the system as a consequence of the purge operation. In general, the autoclave vessel provides a surge capacity to smooth out pressure surges. In the case of plug in the pressure letdown valve, the system pressure increases gradually. This arrangement allows time for corrective action before the safety rupture discs in the system open.

IV-B REACTOR OPERATION

This section discusses the general conditions of startup, run, and shutdown. The functions of reactor components have been described; the mechanics of their control in conduct of experiments is beyond the scope of this report.

The time needed to start up and line out (establish various steady state conditions before experimental samples are taken) is considerable. Consequently, it is not economical to start up for a single sample. Furthermore, when an operating condition is changed, time must be allowed for the effect of the change to line out; and this delays sample collection accordingly.

Laboratory experiments vary in length from about one day to one week. Laboratory work needed for reactor control is carried out during the run, and so are gas analyses. The workup of liquid products may be partially performed during the run, or may be deferred, according to time available. The conduct of experiments with the continuous reactor therefore demands a period of intense effort which is followed by a considerably longer period for routine workup and analysis of product materials.

IV-B-1 Startup

At startup the reactor has been left filled with flush oil from the previous experiment. This expedient avoids exposing coal and solvent to heat for a prolonged period while the reactor cools, and hence to a situation in which partially processed coal or minerals may settle and plug the preheater tubing.

The first step is to fill the suction reservoir (figure 2) with hydrogen and adjust the back pressure regulator to the desired operating pressure; if necessary, the needle metering valve is set to deliver the desired volume of gas per unit time. These gas metering adjustments, made by trial, are completed the day before the experiment.

The next step is to turn on the heaters and pumps to circulate flush oil while operating temperatures are adjusted. During this period the flow of reducing gas is also started. The specified operating temperatures, flow rates, and operating pressures are usually obtained within three hours.

This initial lineout period affords time to prepare feed slurry. Cans of solvent are placed in a drying oven, at 75-100° C for anthracene oil, where crystalline material is melted. Partially used cans may be kept warm until used, or reheated and mixed if allowed to cool. The same stock provides oil for flushing and for slurry; in both uses the oil is thoroughly mixed before any is removed. A stainless steel beaker is weighed; and oil is added to the weight desired, with a precision of about 1 g in total weights of 2-4 kg. The charge of powdered coal is weighed with similar precision, carefully scooped into the beaker, and blended by spatula to work out air in the wetted powder. The mixing adds considerable air, which must be eliminated before the feed pump can perform reliably. A motor-driven stirrer assists in air removal (stirring is required for about half an hour at moderate rates); air is more fully eliminated when the slurry is heated above operating temperature and allowed to cool to the temperature desired. This temperature has an effect on the behavior of the feed pump. The viscosity of the oil determines the size opening between ball check and seat as the pump operates. For anthracene oil, the slurry pot temperature is above the point at which oil may tend to crystallize. In long runs, makeup batches of slurry must be added to the feed vessel with care to avoid mixing in air bubbles, which is facilitated by adding before residual slurry drops to two kilograms, and by bringing new slurry to a matching temperature.

IV-B-2 Run

At the end of the condition lineout, feed slurry is substituted for flush oil. No product is collected for some considerable time; the initial coal solution mixes with flush oil, and the back mixing dilutes it progressively; so that several reactor volumes are made before flush oil is eliminated. Gas is vented and lineout slurry goes to the slop vessel (figure 4). (So-called "lineout" products during this period on coal solution may be taken for measurements, described in section IV-D, which govern the decision to conclude lineout, or which indicate a need to await effects of an operating change.) The entire procedure is intended to insure that a valid sample is collected from reacted feed slurry, with no admixture of flush oil.

A sample of product solution is collected for a timed interval. Toward the end of this interval, perhaps the last 45 minutes, a gas sample is collected; this segment is selected to insure that air in the sample flask has been completely flushed out before product gas is sampled. Several sets of operating conditions may be studied before shutdown, with one or more samples collected for each. If products are not taken, the liquid is diverted to the slop vessel and gas is vented (figure 4) by means of control valves.

IV-B-3 Shutdown

After the final sample, feed slurry is replaced by flush oil for shutdown. Heaters are turned off, but pumping continues until the reactor cools; when appreciable reaction can no longer take place, the gas flow is also stopped. Pumping continues until the reactor temperature is below 200°C.

IV-B-4 Concurrent Operations

Throughout the run, the operator records certain data and makes indicated adjustments. The most important data recorded are:

1. Feed rate - measured by recording scale readings at 15-minute intervals and computed on an hourly basis
2. Temperatures of preheater and dissolver - recorded continuously and observed by the operator
3. Pressure readings across needle metering valve - recorded continuously; the operator confirms that values remain the same as those at the calibration of gas flow
4. Start time for liquid sample period, with slurry weight, nitrogen purge pressure and volume, and a verification that temperature and pressure readings are at specified values

5. Start time for gas sample period

6. Stop times for sample periods, with readings for
   nitrogen pressure and volume,
   scale reading for feed vessel weight

The operator adjusts feed rate by changing the length of the piston stroke in the high pressure feed pump. He takes a feed slurry sample from the recycle loop at the beginning and at the end of each liquid sample period. He adjusts temperatures by variac and controller settings. Following each liquid sample collection, the operator removes the sample flask from the system and stoppers it; he also drains water from the knockout vessel into a weighed bottle and weighs it. The operator takes the gas sample bag to the laboratory for analysis of the gas and measurement of the gas volume.

IV-B-5 Laboratory Procedures for Control of Feed Slurry

Feed slurry is prepared from materials analyzed to establish their composition: a coal ground to a controlled particle size distribution and a well-characterized solvent, in accurately weighed amounts. The average initial composition is presumably known. However, coal or coal and mineral phases settle in the feed vessel, water evaporates from the feed vessel, and some of the solvent evaporates also. To maintain a uniform slurry of correct composition over an extended period, and to draw this suspension down to small residual volumes without affecting the average composition, various procedures are adopted. The methods of stirring slurry, warming the feed vessel, and returning circulated slurry down the dip tube to reduce the mixing with air, have been mentioned. Feed slurry composition is monitored by periodic ash analysis and by occasionally drawing samples for water determination if the feed coal contains a significant amount (excess of 2 or 3%) of water.

To estimate the amount of coal in a slurry, a weighed sample is taken from the slurry recycle loop, ashed for a measure of mineral content, and compared with the ash in feed coal. For a 2:1 solvent to coal ratio, ash from a slurry sample should be 1/3 the concentration in feed coal if the suspension is good. When stirring is marginal, samples tend to increase in ash as slurry is used up, or to run below theory if taken from a full pot.

The Karl Fischer method for determination of water is adapted for use in analyzing feed slurry for water. Slurry is sampled by inserting a small bottle in the return stream to collect 10-20 g from the slurry recycle loop. Feed slurry is also inspected for density; it has also been tested for evaporation rates in the light oils. All of these procedures for control of feed slurry are detailed in OCR Interim Report No. 7.

IV-B-6 Lineout Control

One general problem in experiments with the reactor is to develop methods which establish the reproducibility of the product, methods which can indicate when the product is equilibrated with feeds and with the effect of reaction conditions. Four such methods are mentioned here; details of the analyses are given in section IV-D along with product analyses.

In early studies it was observed that the infrared spectrum of a coal solution had several bands whose relative intensity had altered from similar bands in the initial solvent. The absorbance ratio of bands at 3.28 microns and 3.42 microns changed progressively after the switch from flush solvent to feed slurry. For comparison of samples, the ratio of absorbance for the 3.42 micron band divided by the absorbance at the 3.28 micron band is computed. The ratio, called $\overline{IR}$ hereafter, is plotted as a function of operating time. The $\overline{IR}$ ratio for raw anthracene oil is smaller in the initial flush oil than in the lined out sample, which has been hydrogenated during the reaction and also had hydrogen components added from the dissolving coal. Because the mineral phase in the coal exerts a catalytic influence on product composition, the settling of mineral in the reactor causes long swings in reactivity; minerals may settle, then classify by gravity separation processes. In this condition the reactivity oscillates periodically; a lined out reactor produces slightly different composition products from time to time because of this mechanism.

A "blackness" test is also applied to coal solutions. The absorbance of light by coal solutions in pyridine, when observed by a spectrophotometer, provides a rapid method for measuring a property of a coal solution which relates to the concentration and reduction state of coal dissolved in the solution. The color can be related to the absorbance by a colorimetric factor to yield this concentration. Within observation limits, it is a sensitive index of the state of the product in the reactor.

Ash analysis is a third method of observing lineout. If the concentration of mineral in the coal solution should account for all of the mineral fed into the reactor, presumably the product solution would be fully lined out. But sampling is difficult since mineral settles, and resuspending it for a representative sample is awkward. If an entire product sample is filtered and the residue ignited to determine the ash present, the finest mineral matter will have passed through even fine analytical paper.

With small samples, it is preferable to ash the whole sample. An alternative procedure is to collect a reasonable volume of sample, warm it, and stir it properly while subsamples are removed for ash analysis; this is the same analysis as is used for slurry feed. Precise duplicate values are reasonable evidence of reliability in the samples ashed. The buildup of mineral in the product solution, as noted with the $\overline{\text{IR}}$ measurements, is influenced by the tendency of mineral to settle in the dissolver; and times required for equilibration of mineral may differ readily from time required for equilibration of the organic phases.

Assuming that iron is catalytic, the concentration of iron must reach steady state in the dissolver before the reactor can be considered completely lined out. An understanding of mineral behavior appears essential to developing the most reliable results possible. In run CU 48, the first sample was taken after a normal lineout interval, the second after an extended lineout interval. Changes between samples could indicate the effect of changes in mineral concentration or composition in the dissolver.

The composition of gaseous products is a good method of observing approaching lineout. The appearance of hydrogen sulfide especially and its change as a function of operating time follow a repeatable pattern. However, gas composition does not relate directly to the amount of pyrite fed, the amount of organic sulfur fed, or the amount of conversion produced. This is because the hydrogen sulfide and carbon dioxide react with traces of ammonia formed and then dissolve in the water condensate. The equilibrium is temperature-dependent and influenced appreciably by minor variations in ammonia yield. These characteristics differ with flash vessels operated at different temperature and pressure conditions. The relations between gas composition, operating conditions, and yield should be more direct in flash vessels operating at higher temperatures and pressures.

Such observations account for some of the difficulty in making complete element-by-element balances; the time required to line out the composition of any given component needs to be satisfied in samples taken.

IV-C WORKUP OF COAL SOLUTION

Along with the gas sample, two others are taken from the reactor to account for all of the feed slurry and hydrogen fed in. The smaller of these, perhaps 0.1% of feed slurry, is water recovered from the knockout vessel between the liquid sample flask and the gas collection bag, water which has condensed in the gas line. Because the weight of sample is so small, this product is normally reported in the water yield, which is largely from the stripping operation. In fact, the knockout vessel water contains traces of oil, as well as ammonium carbonate, ammonium sulfide, and a small amount of phenol. A refinement of yield results by analysis of this fraction is possible, but the influence on overall results would be very small.

This section discusses methods used for evaluation of the liquid product sample. These are separation procedures, conditioned by handling losses which must be accounted in order to afford a handling-loss-free product distribution within the sample. These methods are typical and were employed during the experiment reported in section V.

However, since that time, the modification of equipment and the increase in sample size available from the reactor, refined handling techniques, refined sampling techniques, and accumulated experience, have all reduced the size of corrections required and are a real consideration in reporting results.

Before workup, the coal solution has been collected in a tared, 3-liter, stainless steel, round bottom flask. Flask and contents have been weighed. The first step in workup of the product solution in the laboratory version of the SRC process (figure 5) is stripping it of water and light oils.

IV-C-1 Stripping

The flask of coal solution is attached to the stripping apparatus shown in figure 6. Stripping is a preliminary vacuum distillation designed to permit recovery of the product without uncontrolled loss of volatile substances in the filtration step which follows. The flask is warmed while vacuum is cautiously applied to preclude bumping or foaming.

The more volatile fraction passing through the condenser as vapor and condensed at dry ice temperature is the cold trap product. The fraction condensed by the water cooled condenser in CU 48 was 0.1 g per sample, included with the cold trap oil. Both products contain both oil and water. The oil and water phases are separated after stripping is stopped at a head temperature of 50°C (later, 100°C, or adjusted as necessary to obtain a balance yield of solvent for recycle).

The vacuum reached by the end of the distillation is $\leq$ 3 mm Hg. The weights of water and cold trap oil are recorded.

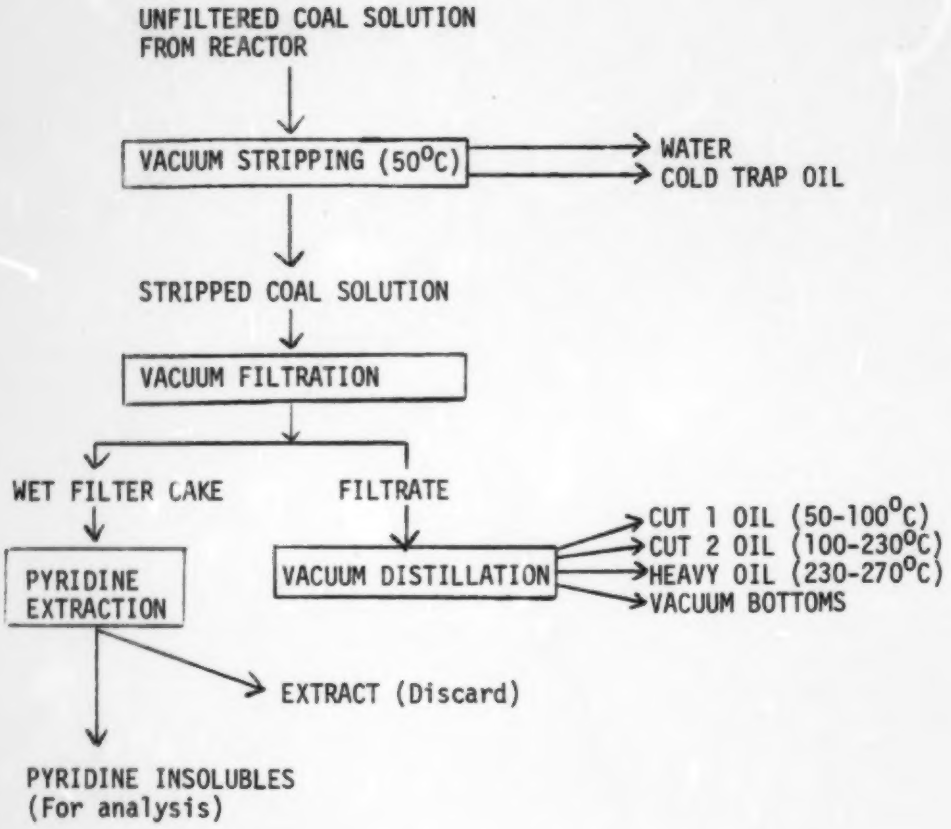

UNFILTERED COAL SOLUTION FROM REACTOR
VACUUM STRIPPING (50°C)
WATER
COLD TRAP OIL
STRIPPED COAL SOLUTION
VACUUM FILTRATION
WET FILTER CAKE
FILTRATE
PYRIDINE EXTRACTION
VACUUM DISTILLATION
CUT 1 OIL (50-100°C)
CUT 2 OIL (100-230°C)
HEAVY OIL (230-270°C)
VACUUM BOTTOMS
EXTRACT (Discard)
PYRIDINE INSOLUBLES (For analysis)

Figure 5 Workup

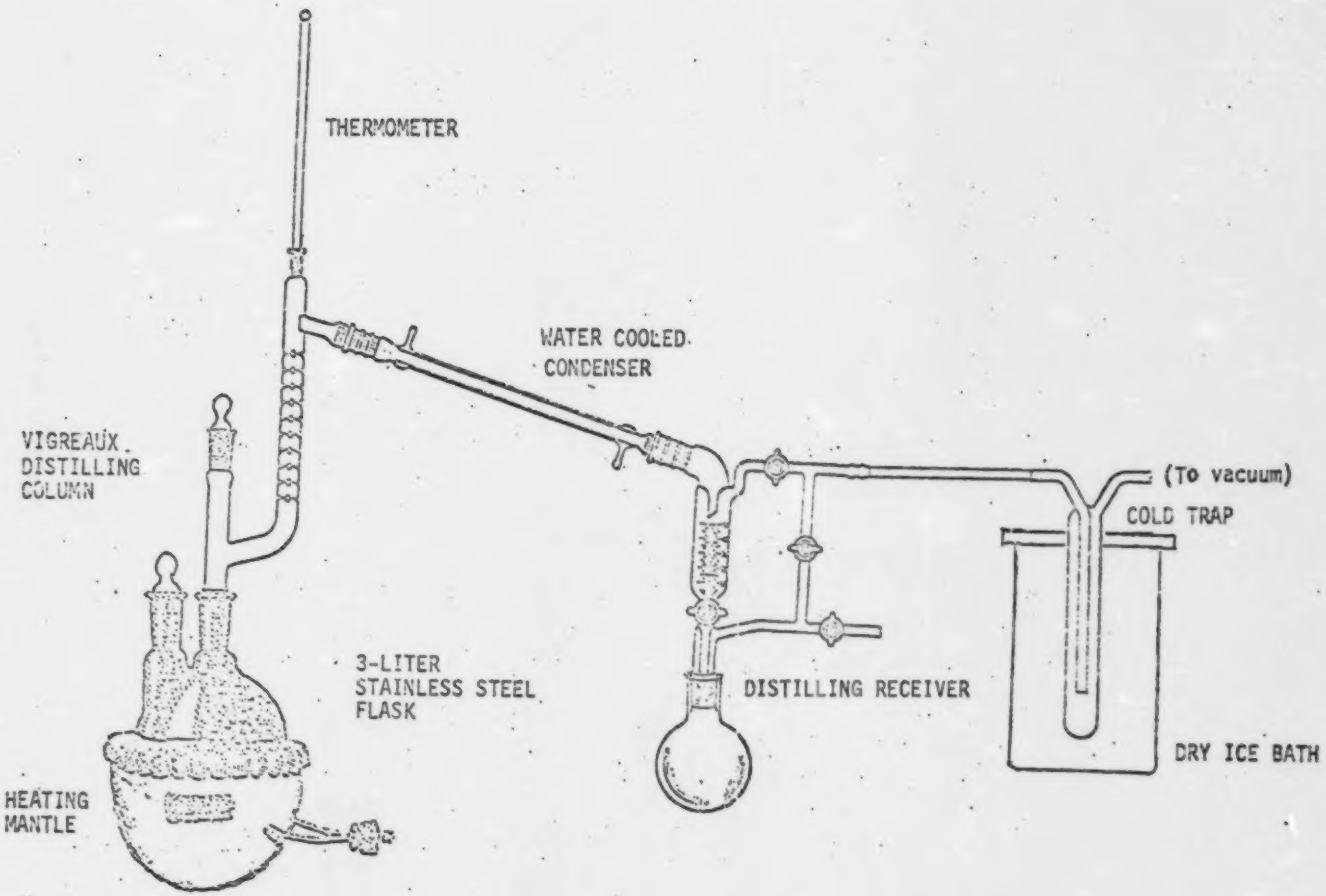

THERMOMETER
WATER COOLED CONDENSER
VIGREAUX DISTILLING COLUMN
3-LITER STAINLESS STEEL FLASK
HEATING MANTLE
DISTILLING RECEIVER
(To vacuum)
COLD TRAP
DRY ICE BATH

Figure 6 Stripping Apparatus

IV-C-2 Filtration

The flask is removed from the stripping apparatus and weighed before filtration. To afford quantitative results, all equipment components (figure 7) for this step are separately weighed: Whatman #4 filter paper, steam-heated Buchner funnel, vacuum adapter which directs the filtrate, and round bottom receiver flask containing five small boiling stones.

Sometimes a measured amount of cut 1 oil is applied to the filter paper, enough to hold it in place over funnel orifices. This procedure has been adopted because solution occasionally passed under the paper when dry. Sometimes also a cold trap is inserted in the vacuum line to condense volatiles which escape the filtrate. Since the condensate is less than 1 g, this practice was later abandoned. However, during CU 48, the collection of cold trap condensate was made.

The hot stripped solution is poured into the funnel, under a vacuum of approximately 90 mm Hg. When drained, the collection flask is reweighed for a record of material filtered and material held up by walls of the flask.

The products are a filtrate and a wet filter cake. The receiver flask is weighed again to obtain weight of filtrate. The cake, perhaps 0.32 to 0.64 cm (1/8 to 1/4 inch thick), is removed from the funnel and weighed as a unit with the filter paper; usually these make a compact unit which can be handled without difficulty. Finally, the funnel and associated glassware are weighed to establish transfer losses. (In later work, the funnel has not been weighed nor cleaned since a fairly constant holdup in the funnel is demonstrated; however, small

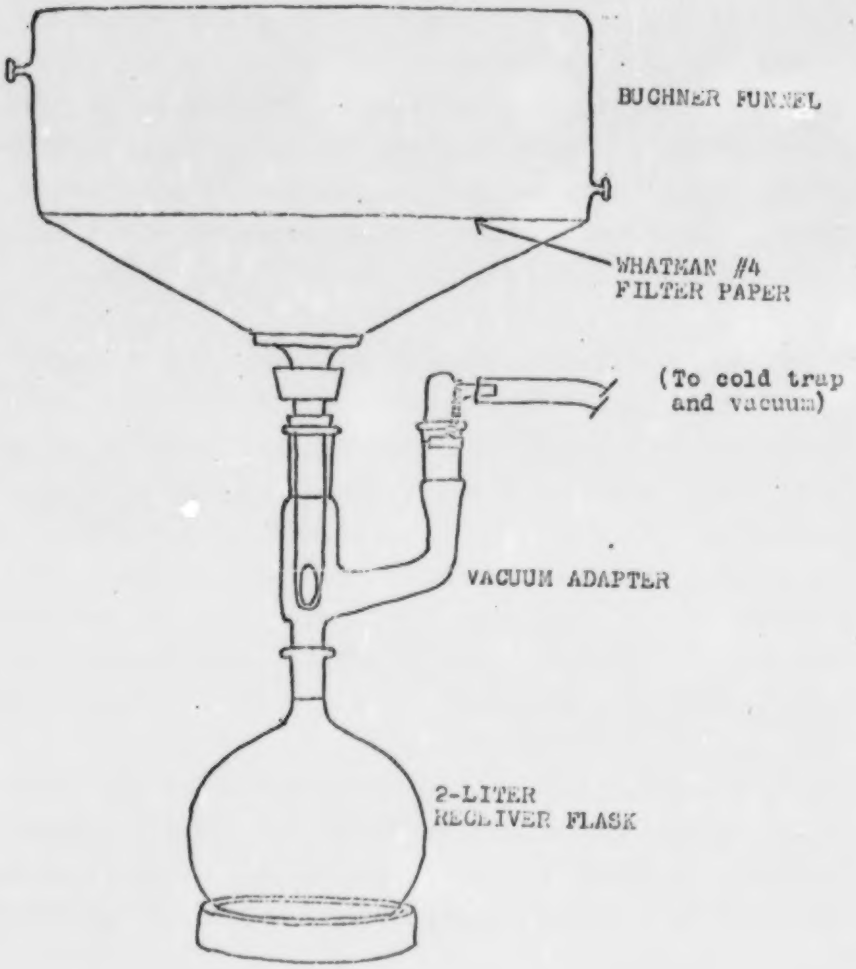

BUCHNER FUNNEL
WHATMAN #4
FILTER PAPER
(To cold trap
and vacuum)
VACUUM ADAPTER
2-LITER
RECEIVER FLASK

Figure 7 Filtration Equipment

variations in holdup occasionally give an output weight more than input weight.) As a check, the weights of wet filter cake, filtrate, and transfer losses are summed for comparison with the weight of stripped liquid transferred from the original collection flask.

Wet filter cake is removed from the paper and bottled for further workup.

IV-C-3 Distillation for Solvent Recovery

The filtrate contains both solvent and vacuum bottoms, or solvent refined coal. These are separated by distillation with equipment used for stripping (figure 6). Distillate is collected in a 1- or 2-liter flask. For experiment CU 48, "cut 1" oil is that fraction distilling between 50 and 100° at less than 3mm Hg; solvent ("cut 2") is the cut distilling between 100 and 230°C at less than 3mm Hg. The use of a fraction collector permits changing receivers without interrupting distillation. Heavy oil, during CU 48, was collected between 230 and 270°C; later, heavy oil was allowed to remain with the vacuum bottoms, although the fraction distilling between 230 and 250°C was included with cut 2 oil. (Cut points in many experiments were arbitrary and might be conditioned by the need to obtain a breakeven quantity of solvent.)

In this second distillation, the cold trap also condenses about 1 g of oil, which is included with cut 1 oil in weighing products. Generally, the weight of input compares well with that of products.

The weights of distillates and residue are obtained by weighing all flasks before and after distillation. As a check, the weights of vacuum bottoms, heavy oil, cut 2 oil, and cut 1 oil are summed and compared with the original weight of sample taken.

Typically, the second distillation is started with a flow of cool water through the condenser. As vapor temperature increases, the distillate tends to solidify. At this point the water flow is cut off and, if necessary, the condenser is drained. Toward the end of distillation, wax-like products often appear in the condenser or fraction collector. To make the distillate flow into the receiver flask, a blast of hot air is directed onto the area affected by an electric heat gun.

Before sampling, cut 2 oil is warmed and mixed to homogenize it. Distillation residue, or vacuum bottoms, is poured while molten into a metal pan, cooled to solidify it, and then broken up and bottled. In CU 48, however, vacuum bottoms were allowed to solidify in the flask, then broken out. This product is carefully ground in a mortar, sieved to remove boiling stones which are necessary to prevent bumping during distillation and thoroughly mixed before analysis.

IV-C-4 Workup of Wet Filter Cake

An aliquot of wet filter cake is taken for analysis. The remainder is sampled for determination of the amount of soluble and insoluble material present.

The insoluble fraction was determined by extraction with pyridine; the insoluble residue was rinsed with benzene, then with acetone, and then dried. The dry residue was weighed.

The soluble material was assumed to be the same composition as filtrate. The insoluble residue is further analyzed by ash analysis for determination of MAF conversion; for CU 48 the insoluble residue was also analyzed completely to obtain C, H, N, S, and ash values.

IV-D ANALYTICAL METHODS

This section describes the analytical techniques applied to feed slurry, product solution, and the gaseous, liquid, and solid products of continuous reactor operation. A summary of these methods for the products is shown in table 1; standard procedures, such as those for determining basic or acidic functions in water, are not detailed here.

IV-D-1 Analysis of Gaseous Products

Toward the end of each sample period in a run, gases are collected for a timed interval, usually 45 minutes, in a rubberized fabric gas bag.

First, an infrared spectrum is obtained for each gas sample as a qualitative indication of the gas composition. The quantitative distribution is obtained usually by gas solid chromatography.

Spectra are obtained with a Perkin-Elmer 267 Grating Infrared Spectrophotometer. Either a 5-cm or 10-cm gas cell with sodium chloride windows is used; the smaller cell gives more satisfactory results. The cell is flushed with sample gas and then filled with sample gas to ambient pressure. In very humid weather Irtran-2 windows are used to overcome the problem of water condensing on the windows, but their lower transparency

Table 1. PRODUCT DISTRIBUTION AND ANALYTICAL METHODS

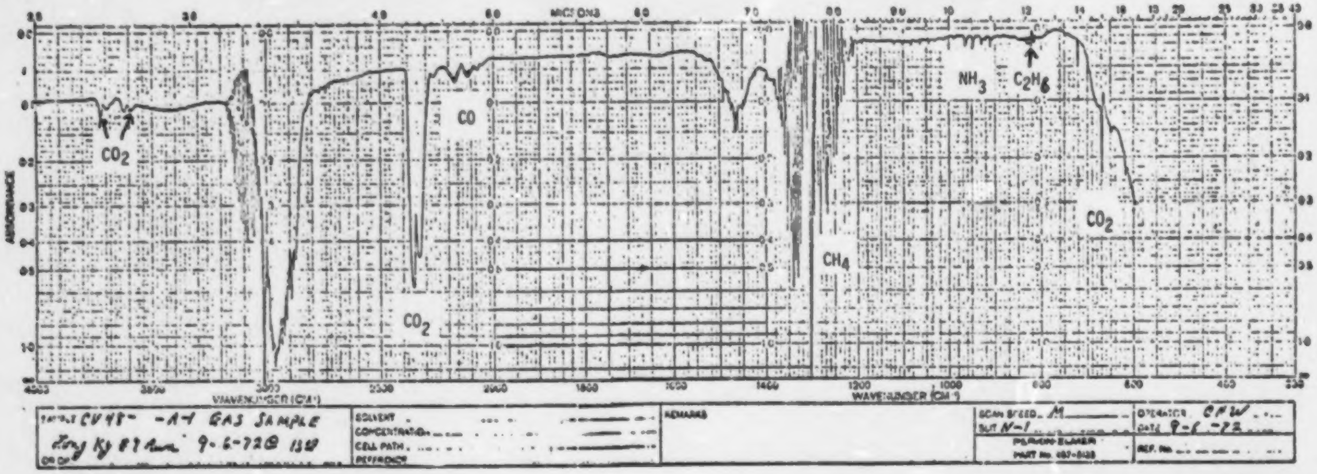
PRODUCT	FRACTION ISOLATED	ANALYSIS AVAILABLE
Gaseous	1. Untreated gas	a. IR spectrum b. H_2S, % c. Molecular weight d. Composition by gas chromatography e. H_2, % (estimated from MW correlation) f. Water (trapped when gas sample is vented)
Liquid	1. Cold trap oil and water	a. Total sulfur, % b. Basic functions c. Acidic functions d. Waste water analyses
	2. Cold trap oil	a. Density b. IR spectrum c. Elemental analysis d. Functional groups
	3. Cut 1 oil (condensate IBP to 100°C @ 3mm Hg)	a. Density b. IR spectrum c. Elemental analysis d. Functional groups
	4. Cut 2 oil (Condensate IBP 100 to 230°C @ 3 mm Hg)	a. Density b. IR spectrum c. Elemental analysis d. Total nitrogen e. Functional groups
	5. Heavy oil (230-270°C @ 3 mm Hg)	a. IR spectrum b. Elemental Analysis
Solid	1. Vacuum distillation residue (vacuum bottoms)	a. Fusion point (gradient bar) b. Elemental analysis c. Ash, % and composition d. Coking properties e. Potential utility specifications
	2. Wet filter cake	a. % pyridine insolubles b. % ash in pyridine insolubles c. Potential utility specifications

requires increased gain settings and gives less satisfactory results. A typical gas product spectrum is shown in figure 8. The areas of interest include the hydrocarbon absorption in the 2800-3200 cm^{-1} region, the carbon dioxide bands 2340-2360 cm^{-1}, and the carbon monoxide bands around 2120-2170 cm^{-1}. Concentrations of methane, carbon dioxide, and carbon monoxide can be estimated, when desired, from the spectrum. In some cases, small amounts of ammonia can be detected by absorption in the region of 900-1000 cm^{-1}.

Second, the volume of hydrogen sulfide is established by withdrawing a sample, such as 500 ml, from the gas bag with a syringe, bubbling it through an ammoniacal zinc sulfate solution to absorb H_2S, and determining the amount iodometrically. The procedure is detailed in appendix A.

Molecular weight of the product gas is determined by the gas density method; a worksheet is illustrated in appendix B. A gas density bulb of thin wall design (figure 9) is used; it can be evacuated and weighed repeatedly within 0.3 mg on a semi-microbalance. The bulb is evacuated to less than 1 mm Hg and weighed. The stopcock is opened to fill the bulb with air, and the bulb is reweighed. It is then reevacuated, reweighed, and filled with product gas and weighed again. The weight of gas and weight of air are determined in triplicate. The ratio of gas weight to air weight times 28.95, the calculated molecular weight for air, provides the molecular weight reported for product gas.

Fourth, the gas composition is generally analyzed by gas solid chromatography. The development of this procedure has been presented in OCR Interim Report No. 6; conditions are listed in appendix C. This analysis provides concentrations of methane, ethane, propane, n-butane, iso-butane, carbon monoxide, carbon dioxide, hydrogen, nitrogen, and oxygen.



Reproduced from best available copy.

Figure 8 IR Spectrum for Product Gas

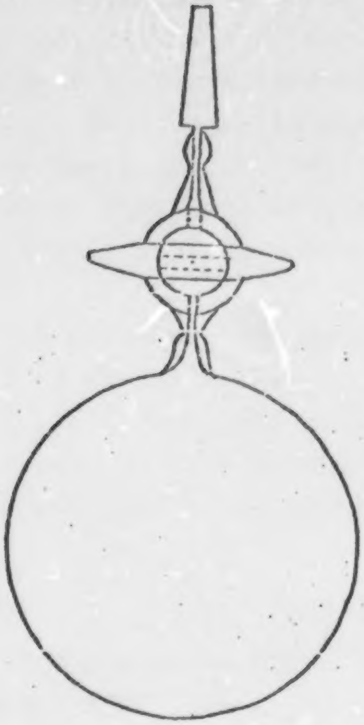


Figure 9 Gas Density Bulb

Water concentration in the output gas is calculated from the weight condensed in the cold trap when gas bag contents are vented later. Results are normalized to 100% by making any required small correction (under 3%) to the hydrogen content. Any oxygen present is presumed to be from air contamination during sampling; therefore, results are corrected for the oxygen content, usually under 0.4%; and the amount of nitrogen which would be associated with this level of oxygen is determined. The results are then reported on a normalized basis. Output gas compositons as determined by gas chromatography for CU 48 are given in section V.

Finally, for mass balance information, the volume of gas collected in the timed interval is determined. Gas remaining in the gas bag is vented through a trap cooled by dry ice to condense water, which is determined by the weight gain in the cold trap, and then through a wet test meter. The gas volumes used in analysis are added to this vented amount to give the total volume which has been collected.

This total may be converted to moles of product gas by multiplying volume of gas in liters by the molar equivalent of one liter of gas at the temperature and pressure of the vented gas. Molar equivalents for one liter of gas in tabular form are shown in appendix A; they may also be calculated from the equation

$$\text{moles/liter} = \frac{P}{760} \times \frac{273}{T} \times \frac{1}{22.40}$$

where P is pressure in mm of Hg and T is temperature in degrees absolute (= °C + 273). The temperature used to establish total gas volume is that from the wet test meter thermometer; the pressure used is ambient barometric, corrected for the vapor pressure of water at the wet test meter temperature. The moles of product gas for the timed interval are then converted to a moles-per-hour figure. The weight of product gas is calculated simply by multiplying moles by molecular weight.

In the mass balance report for CU 48 (section V), total gas output calculated as just described includes unreacted hydrogen, but not nitrogen from the nitrogen purge; in the yields reported, the yield of gas does not include nitrogen, water, or unreacted hydrogen, but only gases arising from the process (hydrocarbons, hydrogen sulfide, carbon monoxide, and carbon dioxide), or total gas weight less hydrogen and nitrogen. Yields of individual gases are not usually reported but are obtained when desired, as with CU 48, from output gas compositions. Examination of product gas compositions shows the bulk of gas yield to be hydrocarbons.

A reasonably good correlation is found between hydrogen concentration in product gas and product gas molecular weight, for the range of conditions of interest here. Hydrogen output in moles is readily calculated from moles of output gas and mole % hydrogen, which is estimated from the molecular weight. Hydrogen consumption is hydrogen in, which is calculated by the method described in section IV-A-1, less hydrogen out. Hydrogen consumption on a moles-per-hour basis is converted to a weight % consumption based on slurry and on raw feed coal.

IV-D-2 Analysis of Feed Slurry and Liquid Products

(a) Feed Slurry --

Slurry is sampled by inserting a small weighed bottle or dish in the return stream from the recycle loop to the feed slurry vessel. Two determinations are routinely made, one for ash and one for water. The ash determination is discussed in section IV-B-6 as a means of establishing lineout. The method is as follows: a weighed platinum evaporation dish is passed rapidly throught the return stream of slurry to collect 5-10 g. Dish and sample are reweighed on an analytical balance to determine exact weight of sample. The dish is placed on a sand bath which is heated by low flame from a Fisher burner; oil can be evaporated without ignition, although burning the oil does not seem to introduce significant error. After most of the volatiles have been removed, the dish is placed just inside the door of a muffle furnace adjusted to operate at 750°C. At this position most residual oil and organic matter in the coal burn off without igniting. Shortly the dish can be moved to the back of the furnace and residual ash ignited. If a deep ash layer is observed, the ash is stirred with a platinum wire to surface any unburned carbonaceous matter. The percentage of ash in feed slurry is reported; for a 2:1 solvent-coal ratio, the % ash in a well suspended slurry will be 1/3 of the % ash in the feed coal.

Water content in feed slurry is determined by adaptation of the Karl Fischer method. The whole slurry sample taken is used for this analysis because the water settles out rather quickly. The tared bottle and sample are weighed accurately on an analytical balance. The sample is transferred, through a powder funnel into a dry 200-ml volumetric flask placed in the hood, by use of a stream of dry pyridine from a wash bottle. The volume of solution is then brought to the mark by adding dry pyridine. The flask is stoppered, and the solution thoroughly mixed and allowed to stand for an hour or so to extract water from the coal. (This procedure seems to remove water effectively from lignite and subbituminous coal, as well as water which may be added to solvent.) Water content varies appreciably in the various grades of reagent grade pyridine; so the grade with lowest water content is chosen when possible.

The following adaptation of the Karl Fischer method for titration of water uses a dead stop indicator and commercially available Karl Fischer reagent. This reagent is put into an automatic buret of 25 ml capacity; the titration

vessel is stirred by a magnetically driven stirring bar. Coal slurry is diluted with reagent grade pyridine, and an aliquot of this solution is titrated. The procedure is scaled for slurries containing about 10% water; changes in detail are needed for different water concentrations or for different sample sizes.

Apparatus:	Automatic buret, 25 ml capacity with 1-liter reservoir
	dead stop indicator and platinum electrodes
	magnetic stirrer and Teflon-coated stirring bars
	3-neck standard taper flask, 200 ml, round bottom (or equivalent airtight titration vessel)
Reagents:	Karl Fischer reagent (Fisher Scientific Co., SOK 3)
	Karl Fischer diluent (Fisher Scientific Co., SOK 5)
	reagent grade pyridine (low water content, or dried over mol sieve)

Procedure:

a. Weigh clean dry sample bottle with cap which will contain 20 ml of liquid. Record weight. With slurry pump running, collect 10-20 g of slurry. Cap bottle and reweigh to determine amount of sample taken.

b. Dilute slurry with dry reagent grade pyridine and transfer quantitatively to 200 ml volumetric flask. Fill to the mark with dry pyridine and stopper flask. Mix contents of flask thoroughly and allow flask to stand, with occasional remixing for about an hour. Allow powdered coal to settle out after final remixing.

c. Put about 75 ml of Karl Fischer diluent in titration vessel. Titrate until microammeter of dead stop indicator reads a constant 50-60 microampere current. Pipet 25 ml of dry pyridine into titration vessel, and titrate with Karl Fischer reagent to establish a blank for pyridine. The end point is taken when the same indicator current is obtained as originally used to pre-titrate the solvent.

d. Use 10 ml pipet to transfer solution from 200 ml volumetric flask to 100 ml volumetric flask. Dilute with dry pyridine and adjust to the mark. Mix thoroughly.

e. Transfer 10 ml of solution from second flask to titration vessel. Titrate to same indicator current used to pre-titrate the solvent. Depending on exact water content, the aliquot which can be titrated with one buret of reagent may allow use of a larger pipet. With a titer of 1.0 mg of water per ml, the 10 ml pipet is a suitable volume, assuming the original sample contained 10% water.

f. The reagent blank must be calculated in proportion to the sample taken for titration, compared to the 25 ml portion of dry pyridine used in the blank determination. Since the same pyridine is used for all dilutions, its contribution to the water content remains constant in concentration. Thus the water content of the solvent is proportional to the sample taken.

Use the following procedure for standardization of the reagent:

Weigh a 200 ml volumetric flask on an analytical balance. Add about 250 mg of distilled water. Stopper the flask and reweigh to determine the exact weight of water taken. Dilute to the mark with dry pyridine and mix thoroughly. Titrate 10 or 15 ml aliquots of this solution, adding the solution to pretitrated solvent as described in the determination above. Calculate the titer in milligrams of water per ml of reagent.

$$\text{Titer} = \frac{\dfrac{(\text{mg of water taken})\ (\text{ml of sample})}{200}}{(\text{ml of reagent} - \text{ml of blank})}$$

Calculate the sample as follows:

$$\%H_2O = \frac{(\text{ml of reagent} - \text{ml of blank})\ (\text{titer})(100)}{\text{sample size in mg}}$$

Note: Sample size is $$\frac{\text{Total Sample } (V_1)(V_2)}{(F_1)(F_2)}$$

where V_1 and V_2 are pipet volumes taken and F_1 and F_2 are the sizes of the volumetric flask used in the dulution sequence.

Since it is necessary to titrate a 25 ml portion of the pyridine to determine the water blank for the reagent, the pyridine must be dried for any amount of reagent more than a few milliliters. The most convenient means is to pass the pyridine through a column of molecular sieve. A suitable apparatus for this procedure consists of a 76-cm (30-inch) length of 2.54-cm (1-inch) ID tubing sealed to a flask which will hold 2 liters of liquid. The lower end of the column is closed by a Teflon stopcock and filled with Linde type 4A molecular sieve. The reservoir is filled with reagent grade pyridine, and the stopcock adjusted to permit pyridine to trickle through at about 5 ml a minute; dry pyridine is collected in a clean dry reagent bottle. A column of well activated molecular sieve of this size will process a 3.7-liter (8-pint) bottle. The reagent blank for the dry material should be only 2-3 ml of Karl Fischer reagent for 25 ml of dry pyridine.

The slurry sample to be titrated is dark colored, which necessitates use of an electrical device to locate the end point; and for this the conventional dead stop indicator is satisfactory. In the procedure given, the original sample is diluted in a volumetric flask and mixed before an aliquot is taken for dilution in a second volumetric flask; obviously various combinations of aliquot and volumetric flask volumes may be used to obtain suitable samples for titration. To draw samples within narrow weight ranges is difficult, and variation in sample size must be compensated by the dilution sequence or variation in the amount finally taken for titration. In a small pipet, powdered coal may plug the tip; precision is improved by using larger volumes.

(b) Product Solution --
The unstripped coal solution (liquid sample) is monitored during the run. The infrared spectrum is measured, as for other oils (section IV-D-2-d). A weighed sample of solution is also examined by visible spectrophotometry for a quality called "blackness."

The sample is diluted to a measured volume with pyridine, thoroughly mixed, and filtered. The absorbance of the filtered solution is read in a 1.72 cm (1/2-inch) cell with pyridine in a similar cell for the reference, in a Bausch and Lomb Spectronic 20 Colorimeter. Since the relative intensity of various wavelengths does not change greatly from solution to solution and absorbance in the 400 to 700 nanometer region declines along a smooth curve, the absorbance at 550 nanometers was arbitrarily chosen for one-point comparisons.

blackness = absorbance per gram of coal solution per 100 ml, measured in 1/2-inch cell at 550 nanometers

Blackness and $\overline{IR}$ in combination have been correlated with vacuum bottoms concentration, but the relationship is complex and not fully understood. As a sensitive and reproducible measurement, blackness is useful to indicate whether a reaction is lined out or not. Blackness values exhibit a continuing drift until lineout. As all compositions reach steady state, blackness values become stabilized but exhibit small changes in response to mineral changes in reactor drifts. This oscillation may be caused by temperature, pressure, feed rate, or catalytic changes within the limits of reproducibility of the controls.

(c) Water Phases --
Liquid products are categorized as water phases and oil phases. Most water is isolated in the cold trap during stripping; some condenses and forms a separable phase of cut 1 oil, and a much smaller amount is obtained from the knockout vessel. Water phases are usually combined for analysis; the composite phase is mostly water but does contain sulfide, carbonate, ammonia, and small amounts of phenol (1/2 to 1%).

As water samples age, they turn yellow, indicating the formation of ammonium polysulfide. When yellow solutions are acidified, a whitish precipitate of colloidal sulfur is commonly observed. Sulfur in the water phase is determined as follows. Sodium hydroxide is added to make it alkaline, and hydrogen peroxide is added to insure oxidation of all sulfur to sulfate. The solution is boiled to remove excess hydrogen peroxide and acidified with dilute hydrochloric acid. Sulfate is precipitated by barium chloride.

Ammonia in the water is determined by adding magnesium oxide to a weighed sample in a Kjeldahl flask, distilling the ammonia out, and titrating by the standard Kjeldahl method. By subtracting an assumed amount of phenol, the ammonia, sulfur, and hydrogen are then calculated from the remaining water.

Water trapped from the gas bag and the knockout vessel is usually too small for analyses.

Phenol can be estimated by ultraviolet spectroscopy of acidified water phases.

(d) Light Oils --

Laboratory workup procedures provide two light oils, cold trap oil and cut 1 oil; both are byproducts of the SRC process. As they are removed from the process, a thorough investigation of their composition is not usual. The cut 1 oil in present practice is that cut boiling below 100°C at ≤3 mm Hg during stripping, condensed in the water cooled condenser; during CU 48, however, cut 1 oil was obtained as the fraction boiling below 100°C at ≤3 mm Hg at distillation after filtration. Cold trap oil is collected at -78°C under the same vacuum at stripping. The boiling range of cut 1 oil is within the boiling range of kerosene; the boiling range of cold trap oil is within the boiling range of gasoline.

The density of these oils is measured by weighing in 10 ml volumetric flasks. Their IR spectra are analyzed and their elemental compositions (C, H, S, and N) are established by the methods outlined below for cut 2 oil. However, in the carbon and hydrogen determination of light oils, because of their volatility, the samples are placed in weighed quartz glass capsules instead of the open boat and are distilled more slowly to prevent explosion.

For all oil samples, IR spectra are obtained by either of two methods. By the neat sample method, a few drops of oil are placed on a rock salt plate, covered by a similar plate, and compressed by a brass holder. The oil film must be of reasonably uniform thickness, without water droplets or air bubbles. The spectrum is obtained with the spectrophotometer used in obtaining the IR spectrum for gas (section IV-D-1). Alternatively, the spectrum may be obtained from the sample in solution: a known weight of oil, such as 2.000 g, is transferred to a 100-ml volumetric flask and diluted to the mark by carbon disulfide for a weight/volume concentration of 2.000% (for cold trap oil, a weight/volume solution of 1.000% is better). A rock salt cell of 0.5 mm thickness is filled with the solution; this and a matching reference cell containing only carbon disulfide are placed in the spectrometer. Representative IR spectra for cut 2 oil and other materials for CU 48 are illustrated in appendixes E through I.

A quantity termed the $\overline{\text{IR}}$ ratio is determined by a method described in the Division of Fuel Chemistry Preprints, American Chemical Society (vol. 16, No. 2, pages 68-72). By the general techniques of quantitative analysis as presented in ASTM E 168, a baseline is drawn from the vicinity of 3800 cm^{-1} to the vicinity of 2000 cm^{-1}. The absorbance of the bands at 2920 cm^{-1} and 3040 cm^{-1} are measured, and the ratio

$$\frac{\text{Absorbance at 2920 cm}^{-1}}{\text{Absorbance at 3050 cm}^{-1}}$$

is calculated. (The $\overline{\text{IR}}$ symbol denotes this ratio, and not the inverse, which is the method of the reference.) This ratio serves for ready comparison of samples.

The $\overline{\text{IR}}$ is useful in evaluating variables in reactor operating conditions. If the coal solution is prepared with raw anthracene oil, the initial $\overline{\text{IR}}$ value may be about 0.56;

as coal derived material dilutes and replaces the initial solvent, the value rises to approximately 0.75. If the coal solution is prepared with a well hydrogenated solvent, the initial $\overline{IR}$ may be higher than the value at lineout, particularly if solutions are made at high operating temperatures and at short retention time in the reactor. The $\overline{IR}$ values may be related to the hydrogen transfer capacity of the solvent; but as coal derived material is added to the system, a significant amount of saturated structures is introduced, and these interfere with the observation of transfer reactions. With only IR spectra as a basis for analysis, it is not possible to resolve the hydroaromatic contributions from the contribution of the saturated functions.

$\overline{IR}$ values have a separate use after reactor lineout. The mineral phase in the coal exerts a catalytic influence on product composition. The settling of mineral in the reactor causes long swings in reactivity as minerals settle, then classify by gravity separation processes. In this condition the reactivity oscillates periodically, and a lined out reactor produces material of slightly different composition from time to time in response to this mechanism. In solvent recycle studies, the solvent composition is progressively altered by the addition of oil from the coal and by the thermal decomposition of the original solvent. The observation of $\overline{IR}$ values is useful in recording these long term changes.

(e) Cut 2 Oil --

Cut 2 oil is usually that fraction obtained from distilling filtrate between 100 and 230°C at ≤ 3 mm Hg. When stripping has been stopped at 50°C, the fraction of filtrate distilling between 50 and 100°C is "cut 1" oil and is sometimes included with cut 2 oil for analysis. "Heavy oil" is the fraction distilling between 230 and 270°C for this report; in later practice oil distilling between 230 and 250°C has been included with cut 2 oil, and that distilling above 250°C has been allowed to remain with vacuum bottoms. These cut points will be adjusted in plant operation to obtain the volume of solvent needed for balanced recycle of new slurry.

Besides the $\overline{\mathrm{IR}}$ ratio obtained for cut 2 oil, as described above, this sample is weighed in a 10-ml volumetric flask to establish its density; and its elemental composition is determined as follows.

For the most part, the methods outlined in ASTM D 271 are employed for the carbon, hydrogen, nitrogen, and sulfur determinations. For C and H, the macro combustion train is modified by the substitution of lead peroxide, operated at 185°C, for lead chromate. In addition, a plug of silver screen is used just in front of the copper oxide filling. For increased precision and accuracy, sample weights are increased from the usual 200 mg to 400-500 mg, a modification adding time to the analysis but justified in the improved precision of results for hydrogen. When light oils are analyzed, their volatility produces a risk of forming explosive mixtures, with the chance of blowing the stopper from the combustion tube; consequently, the liquid is placed in a small Vycor tube for weighing and evaporating it in the combustion tube. The higher boiling oils are weighed in conventional Alundum boats of the type used for steel analysis, or in platinum boats; samples burn without difficulty.

Total nitrogen content was routinely determined in oil samples; for run CU 48, the detailed elemental results obtined through the Kjeldahl-ASTM method are reported in section V. Basic nitrogen is obtained by the procedure detailed in appendix D and briefly described here.

For basic nitrogen determination, a 2-g sample of cut 2 oil is weighed in a beaker, to which is added 150 ml acetic acid. Titration equipment consists of:

A Sage Instruments Syringe Pump, model 341, which controls flow rate of titrant solution (0.1 N acetous perchloric acid) into the covered beaker; the beaker is set on

A Labine Magnestir, Cat. No. 1250; electrodes are connected to

A Leeds and Northrup pH meter, set at 1400 mv, connected to

A Sargent Recorder, model SR, set for a chart speed of 2.54 cm (1 inch) per minute

The resulting chart is examined for its inflection point, that point in the middle of the break in the curve where change of slope occurs. The shape of the curve resulting for basic nitrogen determination is similar to that exhibited for the THAM sample in appendix D. The inflection point indicates quantity of titrant required to titrate the sample. Time in minutes is measured between this equivalence point, representing neutralization of the amine in the sample, and the "start" point marked on the chart when the syringe pump started to pump. Basic N concentration in the sample is calculated from time required for titration of the sample and the titer of the titrant in meq/min., which is determined against standard tris (hydroxylmethyl) aminomethane (THAM).

Sulfur determination in cut 2 oil (and other oils) is by the bomb washing method of ASTM D 271. A 1-g sample is weighed into the platinum crucible (or, for the volatile cold trap oil, in a gel capsule) and placed in a Parr bomb with 5 ml distilled water for gas absorption under 30 atmospheres of oxygen. After ignition by the usual wire method, the bomb is cooled in its bath to permit water in the bomb to absorb sulfuric acid. The bomb is thoroughly washed with distilled water. Bromine water is added to the washings, which are boiled to release excess bromine. Sodium hydroxide is added to make the washings slightly alkaline; the washings are filtered to remove metallic hydroxide. Dilute hydrochloric acid is added to acidify the filtrate to a methyl orange indicator. Barium chloride is added to precipitate sulfate as barium sulfate. The solution is digested, filtered, ignited, and weighed, and sulfur is calculated by the standard method.

IV-D-3 Analysis of Solid Products

Solid products are vacuum bottoms and wet filter cake. Most of the basic information for evaluation of both products is provided by elemental analysis (C, H, S, and for CU 48 also N). The ash content is determined for each, and the fusion point for vacuum bottoms.

The methods for carbon and hydrogen are the same adaptations of ASTM D 271 as have been described for liquid products. The method there described for sulfur is also identical, except that a 1-g sample of vacuum bottoms or wet filter cake is melted in the platinum crucible to insure complete combustion at firing of the Parr bomb. The Kjeldahl method is used for nitrogen.

Fusion point for vacuum bottoms samples is customarily obtained only to provide a check on distillation procedures; it permits sample comparison from run to run.

The ash content of vacuum bottoms, ususally 0.1% or less, or of wet filter cake (25-30%) is determined by igniting samples in platinum evaporating dishes. For accuracy, vacuum bottoms samples are relatively large, 5 to 10 g. Wet filter cake samples can be smaller. The dish is placed on a sand bath heated with a Bunsen burner, which drives off volatile matter and causes partial combustion of the sample. The dish is then placed in an electrically heated muffle furnace at 750°C to complete ignition, then cooled and weighed. Residue is reported as ash.

In order to determine the amount of coal converted, wet filter cake is analyzed. A weighed portion is put in a beaker, heated with pyridine, and stirred to extract any solubles. The hot pyridine suspension is filtered and washed with hot pyridine until washings come through colorless, then sequentially rinsed with benzene and acetone. The residue is dried and weighed to determine % pyridine insolubles, which consist of mineral matter (unignited ash) and unconverted carbonaceous material (insoluble organic matter). The % ash is determined on this fraction.

The amount of coal converted to gaseous, liquid, and solid products in the process is determined from pyridine insolubles data. By the Insolubles Difference Method, this is

$$\text{\% feed coal converted} = 100 - \text{\% pyridine insolubles, on loss free basis in reference to feed coal}$$

An alternative method estimates amount of coal converted based on the increased concentration of ash observed in pyridine insolubles. By the Ash Enrichment Method, this is

100 (% ash in feed coal) = (100 - X) (% ash in pyridine insolubles), where X is the % feed coal converted

Both methods are subject to some error. The first depends on quantitative collection of unreacted material; if handling losses are corrected for in the calculation, materials lost must contain the proper ratio of liquids and solids, which is rarely the case. The second method requires that the mineral and carbonaceous material, not dissolved, remain in the proper ratio; settling at any point may segregate mineral preferentially, and this will cause error. The true percentage of coal converted probably lies between results by the two methods.

Since different coals may have different moisture and ash contents, it is often desirable to reduce conversion to the moisture-ash-free or MAF basis; the MAF basis represents the organic fraction of the coal:

$$\%\ \text{MAF conversion} = \frac{(\%\ \text{conversion on feed coal basis})\ (100)}{100 - (\%\ \text{ash} + \%\ \text{moisture})}$$

Both % ash and % moisture are % in feed coal.

SECTION V

RESULTS OF EXPERIMENT CU 48

V-A OBJECTIVES

The objectives of CU 48 were:

1. To demonstrate that the solvent (section V-B-2), which produced an unsatisfactory solution with Elkol coal, would behave in a normal way with Kentucky coal

2. To study the reproducibility of the coal solution production over an extended time; to learn if the solution and product characteristics would match those predicted by interpolation of data acquired through use of the middle fraction of raw anthracene oil as solvent, and through use of a more hydrogenated oil as solvent

3. To prepare samples for detailed elemental balance studies of interest to EPA

4. To prepare materials for use in various projects which require coal derived materials (minerals reclaimed by retorting wet filter cake, for Washington State University; water from cold trap oil and knockout vessel, for Gulf Degremont waste treatment studies)

V-B MATERIALS USED

The four input materials to the reactor are hydrogen, nitrogen, solvent, and coal. The first two are chemically pure gases. The nitrogen purge serves only to prevent other material from plugging lines to pressure gages; it does not affect the reaction (any nitrogen in the products is that released from, or retained in, the coal).

V-B-1 Coal

The coal used was Kentucky #9 from the P&M Colonial Mine near Madisonville, Kentucky. It is ranked as high volatile B bituminous coal. The substantive analysis for the sublot used in the feed slurry in CU 48 is reported on the as-received basis:

Carbon	62.66%	(Macro combustion train method)
Hydrogen	4.22%	(Macro combusition train method; corrected for H in H_2O reported)
Sulfur	4.63%	(Oxygen bomb method)
Nitrogen	1.26%	(Kjeldahl method)
H_2O	3.25%	(Karl Fischer method & oven-drying loss method)
Ash	15.25%	(Ignition at 750°C in platinum)
Oxygen	8.73%	(by difference)
Fe in ash	24.97%	(Ash dissolved in hydrofluoric acid and perchloric acid. Iron determined volumetrically.)

Separate analyses of this sublot revealed small variations in percentage, under 0.5% except for ash content (up to 1%). These differences are explained almost wholly by the procedure which prepared the coal for use.

Mine samples drawn for laboratory use have been more or less uniform and well averaged samples according to the skill and care of the sampler. At the laboratory, the only control of quality of sample which can be exercised is drawing the subsamples carefully. The sample actually used was received in a 55-gallon drum, as run-of-mine in chunks up to 6 inches in diameter. Half of the sample had been removed and used in earlier experiments. When the remainder was used, it was broken up by hand to be accommodated by the grinder and was ground in a Mikro SH Bantam pulverizing mill; a subsample was retained from the ground coal for analysis. The powdered coal was placed in polyethylene bags, sealed, and stored in 5-gallon cans (nominal 10-kg contents), where it had little tendency to gain or lose moisture. Coal for feed slurry makeup was then dipped from a can as it was needed. Analysis of each sublot showed that ash varied from 9.4 to 12% from the average analysis for the first half of sample coal removed from the drum; and in the subsample used for the experiment reported here, the ash content ran quite high (15.25%). This variation in ash content among the subsamples suggests that the mineral and organic phases had not been well mixed. An attempted blending of raw coal in a rolling drum, instead of homogenizing the blend, led to classification with a nonhomogeneous ash distribution and similar variation of ash level in coal used; a more satisfactory processing, ultimately adopted, entailed blending before grinding by the ASTM long pile sampling method, and other improvements.

As a check on the Kjeldahl method of determining nitrogen content in feed coal, the Dumas method was also employed. This was considered necessary because, when all materials were analyzed by the Kjeldahl method, the recovery of nitrogen in coal reaction products exceeded input nitrogen from feed coal and solvent. The obvious cause could be the failure of this method to report all nitrogen in feed coal. Circumstances which cause such failure are often met in analysis of functional groups containing nitrogen; and it is not surprising to meet the difficulty in a complex polymeric system such as coal. The Dumas method, available commercially, is often successful on compounds which do not yield good results in Kjeldahl digestions. While it may still be suspect, it does yield higher values, and thereby suggests the qualitative accuracy of the diagnosis that nitrogen in feed coal is not fully reported by the Kjeldahl analysis. This subject is discussed more fully in section VI-B-2.

At the time the Dumas analyses were obtained for the input coal, it was also resolved that the effect of sample size on nitrogen content reported should be established. The feed coal, well pulverized for microanalysis and considered homogeneous, was therefore analyzed in a range of sample sizes. The results are shown below:

SAMPLE SIZE (mg)	%N
40.345	1.25
34.928	1.30
30.460	1.37
20.290	1.39
13.461	1.64
13.772	1.51

This range of values, rather larger than the usual precision of the Dumas procedure allows, may demonstrate a real effect of sample size on value. It was assumed, anyway, that the larger samples deposit larger amounts of coke residues which retain nitrogen. If this assumption were correct, it would be reasonable to plot all data and extrapolate to zero sample size for an estimate of the probable % N in the feed coal. Figure 10 plots these data; the precision of the analysis is suggested by data at 13 mg, where the band bounded by two straight lines including all data has a mean deviation of 0.065%. The center of the band at zero sample size may be taken as average value, or 1.79% ± 0.04% N. The average dry basis N would be 1.88%.

V-B-2 Solvent

The solvent used was taken from a blend of solvents reclaimed from earlier experiments. This blend had been prepared as a 150-gallon batch for future work as follows.

In preparation for run CU 40, three 55-gallon drums of raw anthracene oil had been distilled at atmospheric and reduced pressure to obtain the 550-800°F middle fraction. After heating

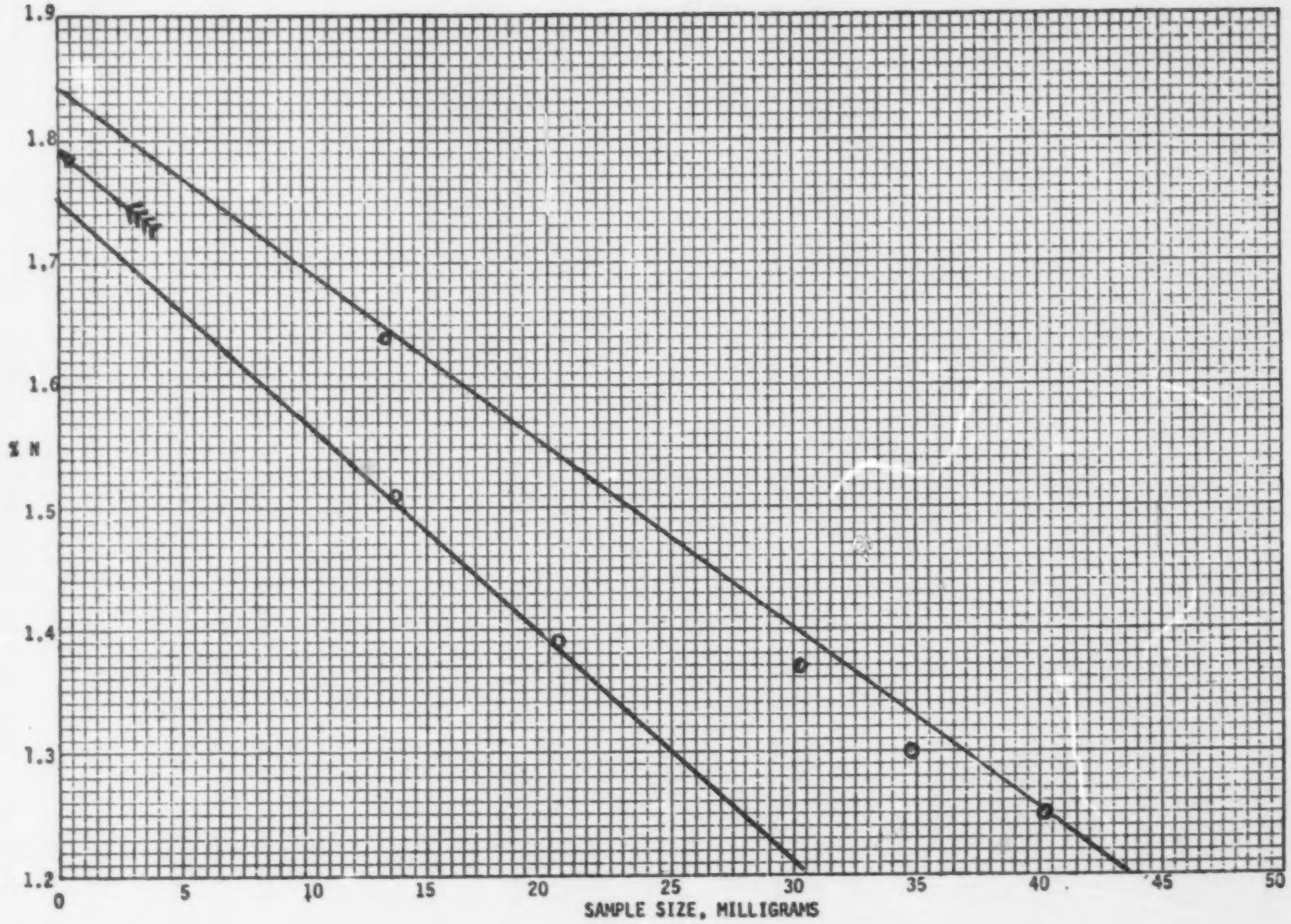


Figure 10 Nitrogen in Feed Coal (Dumas Method)

and blending of the middle fractions, received as three separate cuts, the distillation range for the blend was 70-256°C at 3 mm Hg; about 93% was within the desired range of 100-230°C. This middle fraction raw anthracene oil (MFRAO) had been found suitable in many of its characteristics for reactor operating conditions which would remove sulfur from coal efficiently.

CU 40 was a hydrogenation run; that is, it was an operation in which only oil and hydrogen were admitted to the reactor, for the purpose of adjusting the hydrogen content of the oil. A concentration of 6.04% hydrogen would be near the equilibrium hydrogen content estimated for an anthracene oil solvent in single-pass steady state equilibrium with Kentucky #9 coal in a reactor under 1000 psig hydrogen pressure. For this run the reactor configuration and operating conditions were therefore modified as follows.

The dissolver vessel of the reactor was dismantled and cleaned out. A wire mesh basket about 1-1/2 inches in diameter and 14 inches long was made from fine mesh stainless steel screen. This just filled the volume of the dissolver vessel. The basket was filled with 150 grams of NALCOMO 471 cobalt-molybdenum-alumina extruded catalyst (1/16- x 1/8-inch extrudates). The preheater was made double the normal length and the pumping heads were modified to allow pump rates of up to 10 kilograms of feed oil per hour. In order to simplify feeding of larger amounts of oil, the slurry recycle pump was arranged to draw oil directly from a 55-gallon drum of material. The drum was heated electrically to maintain a temperature over 73°C, the point at which all crystalline material appeared to melt in a laboratory test. Crystalline material was present in this lot of anthracene oil because it had not been fully weathered at the time it was needed for use. This material was less fluid and generally more difficult to process than the raw anthracene oil stock used previously.

The reactor was started with a hydrogen pressure of 1000 psig, and the operating temperatures were slowly advanced to start the reaction. Samples were taken for measurement of infrared spectra to control the hydrogenation reaction. The sand bed for the preheater was advanced to 450°C (although at these flow rates it is likely that the fluid in the preheater did not reach this temperature). With catalyst bed temperatures ranging from 360°C upward to 430°C, the reaction with hydrogen progressed at useful rates. Feed rates, temperatures, and hydrogen pressures were varied as required to produce liquid product with an $\overline{IR}$ of about 0.77. Samples were taken about every two hours for inspection by infrared, and the operating variables were adjusted as required to produce material with the desired composition. In several instances the reactor was upset, and the off-specification materials made in these intervals were set aside for use in developing an infrared working curve for solvent analysis.

The materials which were considered usable were blended to make a composite sample. This material consisted of about 120 gallons of hydrogenated stock. About 30 gallons of Pilot Plant Process Reclaim Solvent (LR 2023), which had been retained from previous work, was then added to this stock. This material had an $\overline{IR}$ ratio of 0.83 and was considered suitable for this use. The resulting blend was then filtered through candle filters of about 30 to 40 micron retention to remove any insoluble materials present. Upon cooling it was found that excessive crystalline material was deposited; the filtration was repeated at room temperature to correct this problem.

A sample of the blended oil was then stripped to remove the fraction boiling below 100°C at a nominal pressure less than 3 mm Hg. Analytical data for LR 2023, the anthracene oil fraction processed, and the CU 40 final blend after stripping are as follows:

	Middle Fraction of LR 2023	Middle Fraction of Raw Anthracene Oil (MFRAO)	Stripped, Hydrogenated Middle Fraction of Raw Anthracene Oil (SHMFRAO)
Carbon %	91.07	91.68	90.58
Hydrogen %	6.12	5.77	6.04
Nitrogen %	0.82	0.99	0.60
Sulfur %	0.56	0.54	0.36
Oxygen % (by difference)	1.43	1.02	2.42
Total	100.00	100.00	100.00
H/C Atomic Ratio	0.800	0.75	0.79
$\overline{\text{IR}}$ Ratio	0.83	0.51	0.75

The SHMFRAO was the solvent mixed with coal for the CU 48 experiment reported here.

Some explanation of the rather particular determination of solvent characteristics may be gained from the following discussion. From analysis of many dozen samples of solvents prepared in anthracene oil experiments, it had been possible to construct a working curve useful in assessing the degree of reaction for any given set of operating conditions. Equally important, the same data affords a means of selecting input solvent characteristics or, by extrapolation, the prediction of output solvent characteristics.

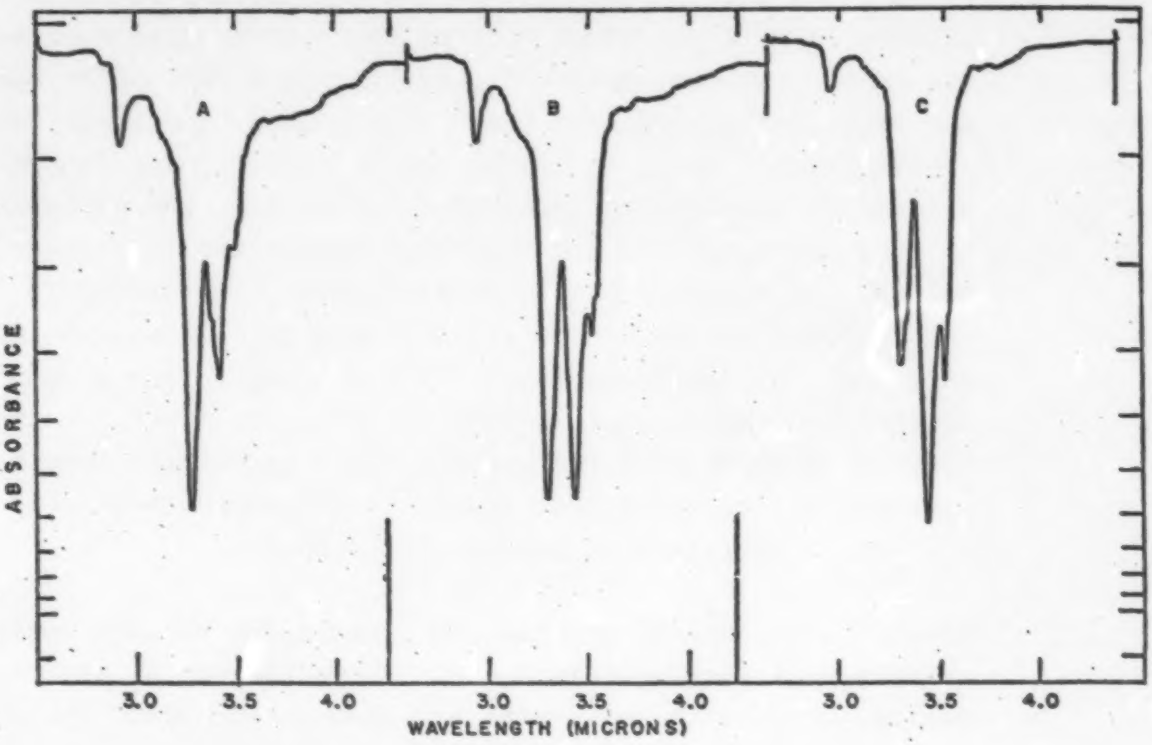
A sample of preliminary calibration data for the development of the working curve is presented below. The $\overline{\text{IR}}$ ratio for product gas and for oils has been discussed (section IV-D). The samples below were run at slow speed on a Perkin Elmer 237 grating spectrophotometer, from which the ratios of absorbance were obtained:

$$\overline{\text{IR}} = \frac{\text{absorbance at 3.41 microns (2933 cm}^{-1}\text{)}}{\text{absorbance at 3.28 microns (3049 cm}^{-1}\text{)}}$$

The relative intensity of these absorbances is found to shift with hydrogenation: raw anthracene oil tends to be lean in hydrogen, and reclaimed solvent contains more hydrogen. In the following data hydrogen was determined by combustion analysis.

Solvent	% C	% H	$\overline{\text{IR}}$ Ratio
Middle fraction, hydrogenated reclaim solvent	91.42	6.901	2.32
Run PA 39 redistilled reclaim solvent	91.38	6.616	1.48
UND 373 reclaim solvent	90.64	6.412	1.26
UND 377 reclaim solvent	90.59	6.428	1.26
UND 376 reclaim solvent	90.85	6.407	1.22
Run PA 74 reclaim solvent	90.46	6.281	0.97
UND 277 reclaim solvent	90.33	6.132	0.94
Run PA 72 reclaim solvent	90.78	6.158	0.85
Continuous Run 2 reclaim solvent	90.65	6.092	0.78
Process Development Plant Run 66 reclaim solvent	90.41	5.987	0.77
Continuous Run 8 reclaim solvent	90.93	5.925	0.75
Run PA 73 reclaim solvent	90.90	6.151	0.74
Continuous Run 11 Sample 17 reclaim solvent	91.35	6.024	0.71
UND anthracene oil redistilled at atmos. press.	90.91	5.916	0.69
Continuous Run 7 reclaim solvent	91.05	5.895	0.65
Continuous Run 12 reclaim solvent	91.20	5.896	0.61
UND 357 reclaim solvent	91.09	5.828	0.57
Middle fraction of raw anthracene oil, sample 1	91.32	5.731	0.56
Middle fraction of raw anthracene oil, sample 2	91.01	5.741	0.56

The change in absorbance with hydrogenation may also be seen in figure 11, which shows the same maximum absorbance in three spectra for comparison of the single strongest band.



A Middle fraction, raw anthracene oil
B Middle fraction, partially hydrogenated
C Middle fraction, hydrogenated reclaim solvent

Figure 11 Effect of Hydrogenation on Absorbance at 3.28 Microns

The 3.28 micron region is predominantly aromatic material. The ratio includes hydroaromatic hydrogen and hydrogen on any saturated radicals as substituents, or any saturated hydrocarbons present as diluents in the solvent at 3.41 microns. In solvents derived from anthracene oil, little saturated diluent is observed since most of the solvent dissolves readily in concentrated sulfuric acid; in cut 2 reclaim solvents the saturated oil is less than 1% by volume, too small to isolate from a typical sample. While the increase in hydrogen can be observed by means of the $\overline{\text{IR}}$ ratio, the difference between hydroaromatic and saturated structures is not resolved. In a single pass, the change in ratio is mostly caused by change in hydroaromatic content; as a solvent is recycled, this is progressively obscured by saturated radicals derived from the coal. (Graphs including ratios for petroleum derived solvents show the hydroaromatic structures completely obscured by saturated radicals.) It therefore remains a problem to isolate this interesting function.

Nevertheless, experience with IR spectra for various solvents affords an almost immediate qualitative picture of the reaction. Quantitative results are also obtainable. The solvents discussed are soluble in carbon tetrachloride or carbon disulfide; the spectra can be run by a solution in one cell with the pure solvent in a matching cell in the reference beam. If equal concentrations of raw solvent solution are placed in one cell and reacted solvent solution in the other, a sophisticated differential measurement is obtained. Here, the gain in hydrogen is linear with increased absorbance at 3.41 microns. The following data, including recycle solvents from autoclave studies, is plotted in figure 12. While most of the scatter may arise from errors inherent in measurements, the last entry in the data below

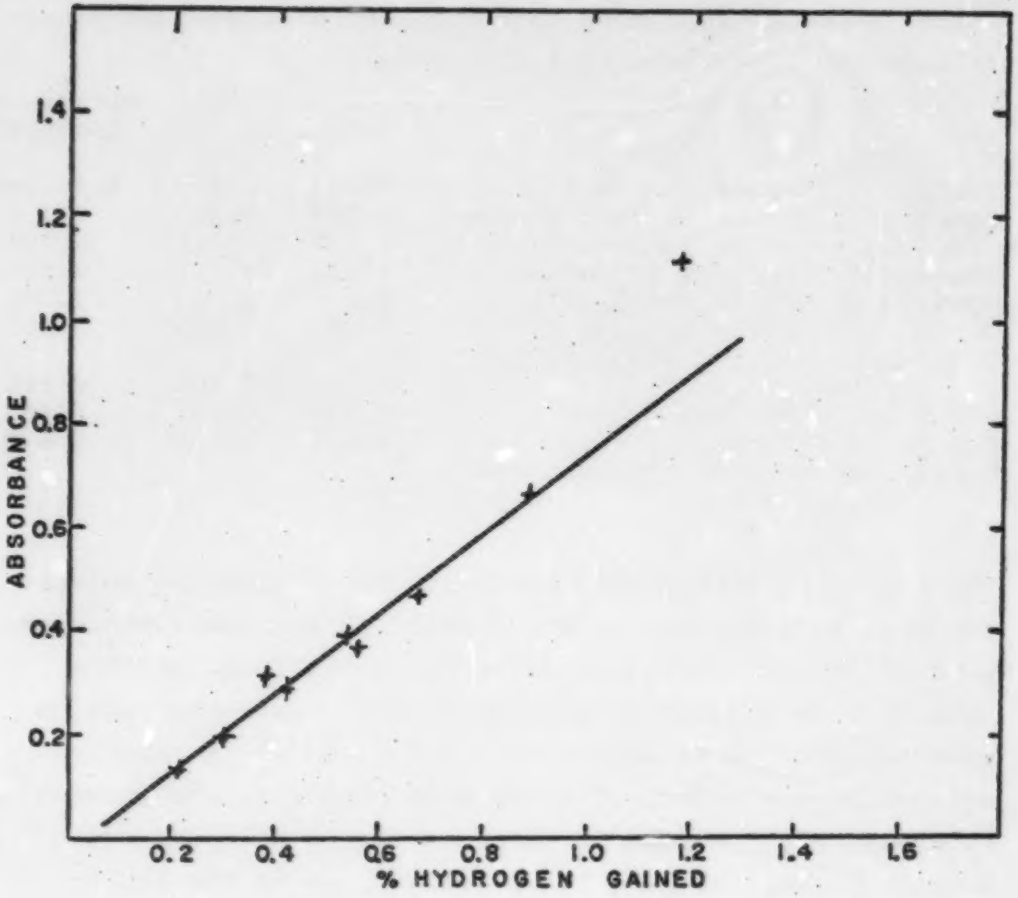


Figure 12 Differential IR Working Curve

represents catalytic hydrogenation under severe conditions. This hydrogenation resulted in removal of sulfur, oxygen, and nitrogen. It also caused formation of alkyl groups, which indicates that more than one kind of structure contributes to absorbance at 3.41 microns.

Solvent	% Hydrogen	Gain in %	Differential Absorbance
Continuous Run 14 Sample 11	5.736	-00-	Reference
Continuous Run 15 reclaim solvent	5.938	0.202	0.125
Continuous Run 11 Sample 17	6.024	0.288	0.195
UND Run 360 reclaim solvent	6.112	0.376	0.314
Continuous Run 18 Sample 7	6.148	0.413	0.298
Run PA 74 reclaim solvent	6.281	0.545	0.362
Continuous Run 19 Sample 40 reclaim solvent	6.267	0.531	0.396
UND Run 376 reclaim solvent	6.407	0.671	0.467
Run PA 39 reclaim solvent	6.616	0.880	0.670
Middle fraction of hydrogenated reclaim solvent	6.901	1.165	1.13

The foregoing data formed the basis for evaluating solvent and coal solutions up to the time of CU 40. $\overline{\text{IR}}$ ratios were plotted for all reclaimed solvents on all runs, and the results were checked by combustion analysis. The results were regarded as estimates of trends, useful in rapidly evaluating the effect of a variable change in the process. Alternatively, changes in the operating conditions could be made to maintain the ratio desired, as in the hydrogenation procedure of CU 40 for solvent production.

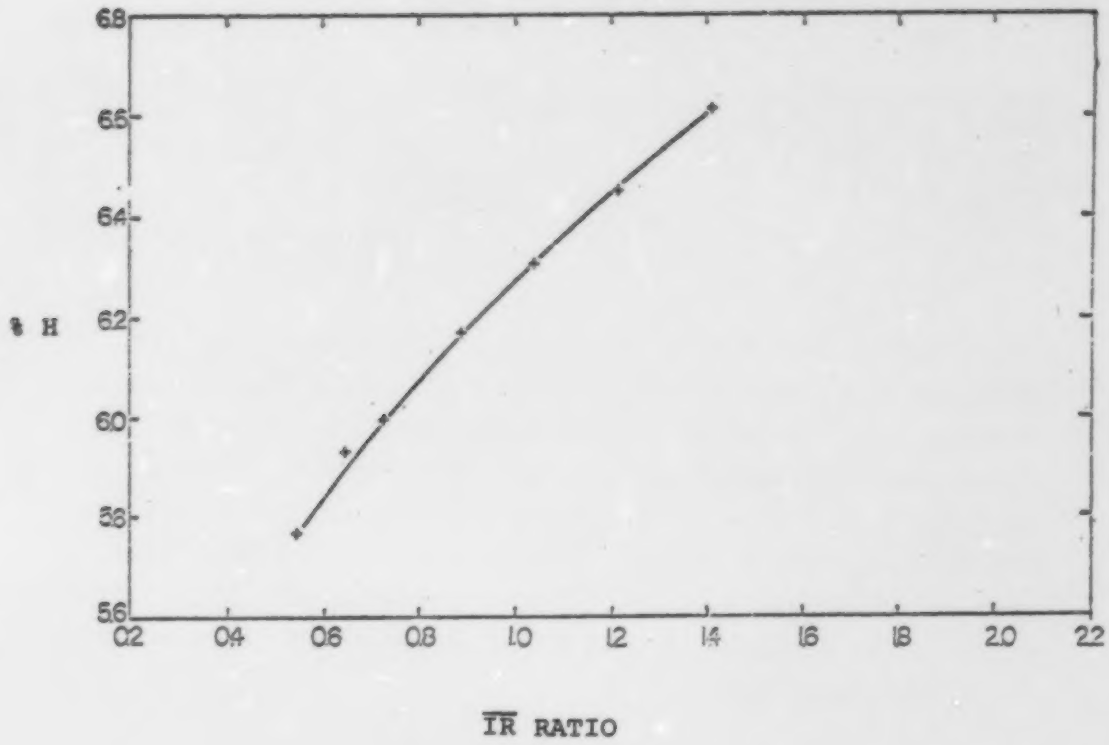
Three samples of the CU 40 production were selected to be the basis for a new working curve: original raw anthracene oil, a moderately hydrogenated product, and a well hydrogenated or over-hydrogenated product. Each was carefully analyzed for carbon and hydrogen; blends were prepared on an analytical balance in large sample weights to minimize blending errors. IR spectra for all material are tabulated below and plotted in figure 13; $\overline{\text{IR}}$ values were computed by dividing measured absorbance at 3.41 microns by measured absorbance at 3.28 microns.

Sample	% C	%H	$\overline{\text{IR}}$
Raw anthracene oil	91.41$\pm$0.16	6.341$\pm$0.008	1.04
Moderately hydrogenated AO	91.60$\mp$0.08	5.770$\mp$0.0001	0.55
Well hydrogenated AO	91.69$\mp$0.18	6.603$\mp$0.076	1.41
Blend 1	Calculated	6.001	0.73
Blend 2	Calculated	5.933	0.66
Blend 3	Calculated	6.169	0.89
Blend 4	Calculated	6.450	1.21

A plot with good fit of points to the average trend is obtained from this blending procedure. For coal solution studies, the reclaimed solvents may contain variable proportions of functional groups or radicals. Here, usually, the ratios of functional groups do not match exactly, and small drifts of data from an averaged line must be expected; but the curve is helpful for inspection of reaction products and is often as accurate as a routine combustion analysis.

V-C REACTOR OPERATION

The operating conditions for CU 48 were chosen to produce a maximum of vacuum bottoms together with effective desulfurization. The operating time for the run was about 40 hours, of which 7 hours was allowed for heating the reactor and bringing slurry feed and reactor contents into a nominal steady state condition. The analytical sample, CU 48A1, was an hour-long collection taken during the ninth hour; CU 48A2 was also an hour-long sample, taken toward the end of the run. The general conditions are summarized in table 2. Hydrogen pressure was 70.3 kg/cm^2 (1000 psig); the coal and solvent analyses are given in section V-B.



$$\overline{\text{IR}} = \frac{\text{Absorbance at 3.41 microns}}{\text{Absorbance at 3.28 microns}}$$

Figure 13 Working Curve, % H in Anthracene Oil Vs. $\overline{\text{IR}}$ Ratio

Table 2. EXPERIMENTAL CONDITIONS

CONDITION	CU 48A1	CU 48A2
Coal	Kentucky No. 9	
Solvent	CU 40B cut 2 oil	
Solvent: coal ratio in feed slurry	2:1	2:1
Reactor pressure, psig	1000	1000
Reactor temperature, °C	450	450
LHSV	1.96	1.96
GHSV	304	304
1/LHSV:hr	0.510	0.510
Solvent:MAF coal:water	2.50:1:0.08	2.50:1:0.05

Table 3. OPERATING DATA

ITEM	CU 48A1	CU 48A2
Blackness of solution	11.65	12.26
$\overline{\text{IR}}$ ratio of feed solvent	0.745	0.745
$\overline{\text{IR}}$ ratio of solution	0.935	0.940
$\overline{\text{IR}}$ ratio of cut 2 reclaim oil	0.744	0.758
% recovery	98.6	99.2
% MAF conversion	82.85	85.09

Table 4. CU 48 YIELDS

	% MOISTURE-ASH-FREE COAL	
MATERIAL	CU 48A1	CU 48A2
Carbon monoxide	0.26	0.23
Carbon dioxide	1.37	1.12
Hydrogen sulfide	2.33	2.32
Hydrocarbon gas	6.54	5.28
Water	2.33	3.60
Excess solvent[a]	2.88	5.36
Vacuum bottoms	68.51	68.12
Insoluble organic matter	17.15	14.91
Total	101.37	100.94

[a] Under the method of reporting, product solvent is not shown; "excess solvent" is that amount exceeding the input quantity. The excess varies considerably with operating conditions and workup techniques, and is significant only to show that solvent for recycle should be available at the operating conditions studied.

During the run occasional $\overline{\text{IR}}$ and blackness checks were made to study the reproducibility of the solution being made. For the samples, these values are included in table 3. Because at room temperature the slurry contained the sticky crystals mentioned earlier, the slurry was heated to 60-70°C. The effect of heating slurry to keep the feed pump system from plugging was probably the loss of some water from the slurry and a small loss of the most volatile solvent fraction.

Except as noted above, the reactor was operated as described in section IV-B. IR spectra for most types of the liquid products are presented in appendix E through I.

V-D YIELDS

Yields (table 4) of most substances followed the expected pattern, but hydrocarbon gases and insoluble organic matter were quite high.

The yield of hydrocarbon gas is largely derived from the solvent; the increase indicates that the input solvent may be less stable than that used earlier (e.g., raw anthracene oil). The difference in behavior may possibly be explained by the increased substitution of saturated radicals and functional groups in the process reclaim solvent blended with CU 40 solvent. For comparison, the composition of the input solvent is shown in table 5 with solvents recovered from samples. The results indicate that the solvent has been brought into balance with respect to net hydrogen, but that some residual reactivity remains. Oxygen elimination and possibly other molecular cleavages consume chemical energy which would otherwise be available to increase the conversion of coal. On the basis

Table 5. CU 48 SOLVENT COMPOSITIONS

CHARACTERISTIC	INPUT SOLVENT (CU 40B Cut 2 Oil)	CUT 2 OIL RECLAIMED	
		CU 48A1	CU 48A2
% Carbon	90.58	91.31	91.73
% Hydrogen	6.04	6.02	6.03
% Nitrogen	0.60	0.765	0.734
% Sulfur	0.36	0.40	0.377
% Oxygen	2.34	1.50	1.129
Total	99.92	99.995	100.000
H/C Atomic Ratio	0.795	0.785	0.783
IR Ratio	0.775	0.766	0.758

of a lower conversion, increased insoluble organic matter would be present at the end of the reaction time allowed.

Duplicate run conditions were compared (CU 28 and CU 48), in which the gas space velocity only was modified (from 304 to 200-230). Results indicated that the reaction is not particularly sensitive to hydrogen flow rate per se. Changes of operating pressure affect the reaction more directly. Generally the yield data appear normal.

V-E GAS ANALYSIS

The product gases are shown in table 6. The difference in distributions is explained in the note. Compared with prior runs, the values are representative for the operating conditions.

V-F ELEMENTAL BALANCES

As a result of efforts to close material balances carefully, duplicate samples were obtained which each accounted for 98% of the input material. Given the solvent composition currently available and operating conditions simulating a Pilot Plant run, the yield pattern should represent that of the Pilot Plant.

Table 6. CU 48 PRODUCT GASES

GAS	MOLECULAR %[a]	
	CU 48A1	CU 48A2
Hydrogen	73.94	77.7
Hydrogen sulfide	3.64	3.09
Nitrogen	5.70	7.19
Methane	9.32	6.46
Ethane	2.91	2.32
Propane	1.45	0.97
n-Butane	0.75	0.53
Isobutane	0.10	0.09
Carbon dioxide	1.68	1.24
Carbon monoxide	0.52	0.40

[a] Normalized on an air- and water-free basis. Sample CU 48A1 was taken in the ninth hour, CU 48A2 about 30 hours later; the gas differences are partially explained by a pressure increase of 1.8 kg/cm^2 (25 psig) later in the run.

The material balance was obtained in steps: balancing feed and primary products, then distributing these primary products in the proper weight ratios as the separations were made. The basic data on worksheets detailed all handling losses and % yield for the various distillation, filtration, and solvent reclaim operations. Materials are first reported on a handling loss-free basis which accounts for all material in the primary reactor samples; finally the weights of these samples are used to adjust the yield pattern to a completely loss-free basis. The adjustment, applied to the weight of liquid product obtained, was prorated in proportion to yield throughout the product distribution obtained in workup of the sample. This final adjustment to loss-free basis required only a small correction, since the primary product sample was good. Products were sampled after filtration and after final separation, as an internal check useful in the study of sampling errors or technique errors in the analytical laboratory.

V-F-1 Accounting for Material Fed

Feed slurry was made by weighing charges of analyzed coal and analyzed solvent, initially 1500 g and 3000 g respectively, on a balance with a precision of ±0.1 g for each. Additions were mixed in substantially the same way to maintain volume in the feed vessel.

The feed vessel was weighed, while an air motor stirred the slurry for uniform feed in the circulation loop to the high pressure pump, on a balance with a precision of ±10 g in weighing 0-20 kg. Since the heat of stirring tended to drive water out of the feed slurry, an accurate feed analysis for water content was needed.

The composition of both coal and solvent has been given in section V-B. The other feed components are hydrogen, fed from a calibrated high pressure system (section IV-A-1), and nitrogen, fed from a Ruska pump to the stirred autoclave (figure 4) as a gage line purge. The weights of gases fed, or number of moles of hydrogen and nitrogen, were determined accurately by application of standard gas law calculations.

Thus, feed components were reduced to weights of materials by measuring weight of slurry and noting sample time during which a constant flow of hydrogen and a measured volume of nitrogen were introduced. The required values for each feed material are expressed in grams. Nitrogen from this source is considered inert in the balance and is therefore not reported.

Feed slurry was sampled at the beginning and at the end of each timed sample period, each was analyzed by the Karl Fischer method for water, and the mean values computed for water content:

CU 48A1	2.05%
CU 48A2	1.46%

For reasons to be discussed, these values are probably incorrect.

V-F-2 Weights of Materials Fed

For the timed one-hour sample intervals, the weights of materials fed in were:

	CU 48A1	CU 48A2
Hydrogen, g	11.2	11.2
Slurry, g	1020.0	1000.0
Slurry composition		
Dry coal, g	332.5	324.9
Solvent, g	687.5	675.1

The input by elements is shown in tables 7 and 8. In these tables the "primary separation" represents the compositions from the sample taken after filtration, the "secondary separation" the compositions from the sample after distillation. Grams of C, H, N, S, ash, and O recovered at each stage are shown with % fed into the reactor. The steps in the elemental balance calculation are listed below.

1. Slurry fed: from preliminary trial calculations it is likely that H_2O in slurry as fed was 0.0% to 1.08% maximum. The best approximation therefore assumes slurry to be made with wet coal at 3.25% H_2O but dried before use. The adjustment slightly alters the weights of coal and oil fed and is calculated as shown.

2. Mineral loss: from preliminary trial calculations it is established that mineral loss occurred. To obtain a sulfur balance, it is essential that the mineral accounting be forced and that product distribution be made with the forced balance yield and product distribution.

Table 7. ELEMENTAL BALANCE, CU 48A1

MATERIAL	WEIGHT (g)	% C	% H	% N	% S	% ASH	% O	C (g)	H (g)	N (g)	S (g)	O (g)	ASH (g)
INPUT - Coal assumed to have 3.25% H_2O; slurry assumed dry when fed													
Coal	332.5	64.76	4.36	1.85	4.94	15.76	8.33	215.3	14.50	6.15	16.43	27.70	52.4
Solvent	687.5	90.58	6.04	1.07	0.36	-	1.95	622.7	41.53	7.36	2.48	13.41	-
Hydrogen	11.2								11.20				
Total	1031.2							838.0	67.23	13.51	18.91	41.1	52.4
PRIMARY SEPARATION - Loss free basis, ash balance forced													
Dry gas	35.9		See table 9					15.14	11.68		5.88	3.13	
H_2O (knockout)	2.6[a]			0.24	0.547		88.9		0.29	0.01	0.01	2.31	
H_2O (cold trap)	23.9[b]	0.57		0.38	0.821		88.0	0.14	2.35	0.09	0.20	21.03	
Cold trap oil	8.0	82.68	12.04	0.212	0.65		4.42	6.61	0.96	0.02	0.05	0.35	
Filtrate	770.3	90.36	6.25	1.17	0.45		1.77	696.04	48.14	9.01	3.47	13.63	
Wet filter cake	190.5	62.32	3.89	1.08	4.70	27.51	0.50	118.72	7.41	2.06	8.95	0.95	52.4
Total	1031.2							836.6	70.83	11.19	18.56	41.40	52.4
% Recovery								99.8	105.3	82.8	98.1	100.7	
SECONDARY SEPARATION - Loss free basis, ash balance forced													
Dry gas	35.9		See table 9					15.14	11.68		5.88	3.13	
H_2O (knockout)	2.6[a]			0.24	0.547		88.9		0.29	0.01	0.01	2.31	
H_2O (cold trap)	23.9[b]	0.57		0.38	0.821		88.0	0.14	2.35	0.09	0.20	21.03	
Cold trap oil	8.0	82.68	12.04	0.212	0.65		4.42	6.61	0.96	0.02	0.05	0.35	
Cut 1 oil	29.9	87.47	7.99	0.0665	0.20		3.67	26.15	2.39	0.20	0.06	1.10	
Cut 2 oil	631.6	91.31	6.02	1.14	0.40		1.13	576.7	38.02	7.20	2.53	7.14	
Heavy oil	15.3	86.35	5.15	1.87	0.815		5.82	3.21	0.79	0.29	0.13	0.89	
Vacuum bottoms	185.5	87.50	5.23	2.20	0.882	0.179	4.01	162.31	9.70	4.08	1.64	7.44	0.33
Pyridine insolubles	98.5	33.61	1.67	0.775	8.68	52.88	2.39	33.10	1.64	0.76	8.54	2.35	52.07
Total	1031.2							833.4	67.82	12.65	19.04	45.74	52.4
% Recovery								99.4	100.9	93.6	100.7	111.3	

a 99% H_2O
b 98% H_2O

Table 8. ELEMENTAL BALANCE, CU 48A2

MATERIAL	WEIGHT (g)	% C	% H	% N	% S	% ASH	% O	C (g)	H (g)	N (g)	S (g)	O (g)	ASH (g)
INPUT - Coal assumed to have 3.25% H_2O; slurry assumed dry when fed													
Coal	324.9	64.76	4.36	1.85	4.94	15.76	8.33	210.4	14.17	6.01	16.05	27.06	51.20
Solvent	675.1	90.58	6.04	1.07	0.36		1.95	611.5	40.78	7.22	2.43	13.16	
Hydrogen	11.2								11.20				
Total	1011.2							821.9	66.15	13.23	18.48	40.22	51.20
PRIMARY SEPARATION - Loss free basis, ash balance forced													
Dry gas	32.2		See table 10					12.08	11.39		5.50	2.52	
H_2O (knockout)	3.6[a]			0.55	1.25		88.0		0.39	0.02	0.05	3.16	
H_2O (cold trap)	19.4[a]	0.57		0.485	0.841		88.0	0.11	2.13	0.09	0.16	17.07	
Cold trap oil	6.8	86.41	11.28	0.219	0.886		1.21	5.88	0.77	0.01	0.06	0.08	
Filtrate	779.4	89.68	5.94	1.28	0.46		2.64	699.00	46.29	9.98	3.58	20.57	
Wet filter cake	169.8	59.27	3.54	1.10	5.14	30.16	0.79	100.64	6.01	1.87	8.73	1.34	51.20
Total	1011.2							817.7	66.98	11.97	18.08	44.74	51.20
% Recovery								99.5	101.2	90.5	97.8	111.2	
SECONDARY SEPARATION - Loss free basis, ash balance forced													
Dry gas	32.2		See table 10					12.08	11.39		5.50	2.52	
H_2O (knockout)	3.6[a]			0.55	1.25		88.0		0.39	0.02	0.05	3.16	
H_2O (cold trap)	19.4[a]	0.57		0.485	0.841		88.0	0.11	2.13	0.09	0.16	17.07	
Cold trap oil	6.8	86.41	11.28	0.219	0.886		1.21	5.88	0.71	0.01	0.06	0.08	
Cut 1 oil	30.9	88.05	7.71	0.69	0.244		3.36	27.21	2.38	0.21	0.08	1.04	
Cut 2 oil	627.6	91.73	6.03	0.91	0.377		0.95	575.7	37.84	5.71	2.37	5.96	
Heavy oil	17.7	87.26	6.24	1.92	0.842		3.74	15.45	1.10	0.34	0.15	0.66	
Vacuum bottoms	182.1	87.32	5.11	2.27	0.944	0.133	4.22	159.00	9.31	4.13	1.72	7.68	0.24
Pyridine insolubles	90.9	32.03	1.73	0.90	9.14	56.07	0.13	29.11	1.57	0.82	8.31	0.12	50.96
Total	1011.2							824.5	66.85	10.71	18.40	38.29	51.20
% Recovery								100.3	101.0	80.9	99.6	95.2	

[a] 98% H_2O

3. Sulfur and nitrogen: selected values are used. For nitrogen, except in water phases and cold trap oil, these are extrapolated Dumas values. Kjeldahl results are shown for cold trap oil, distillation of ammonia from MgO results for water phases. Knockout vessel water and water from the gas sample bag are assumed to have the same composition. NH_3 composition here is calculated as though NH_4SH were present, since only enough sample for the sulfur determination was available.

4. Sulfur results: these are gravimetric sulfurs from oxygen bomb combustions on all low-ash products. High-ash products have been analyzed gravimetrically after Eschka decomposition of samples.

5. Gas compositions: these are slightly revised for calculation of dry volumes and weights. Cold trapped H_2O has been added to H_2O from the knockout vessel and is assumed to have the same composition.

6. Wet filter cake: the weight is computed from the ash content of the filter cake and the theoretical ash input.

7. Pyridine insolubles: the weight is computed from the ash content of the pyridine insolubles and the theoretical ash input.

8. Stripping weights: the weights of gas, water, and oil taken at stripping are taken relative to the whole sample collected. Except for holdup losses in the distillation equipment, these are not corrected.

9. Remainder: the sum of filtrate and wet filter cake must equal the remainder of the whole sample. Thus filtrate is calculated by subtraction of light products and theoretical wet filter cake from the weight of sample to be accounted.

10. The elemental analysis of each product is then entered. The weight of each component element is computed. In most cases, the oxygen by difference closes all accounts, and the sum of

elements reported equals the product weight entered. The gas has a residual of a few grams not acounted for, probably material measured in the gas but not calculated as elemental matter (e.g., oxygen associated with CO and CO_2).

11. Mean values for carbon and hydrogen analyses are shown. Extrapolated Dumas nitrogen values for most samples are shown; data for input solvent scatter, and an average nitrogen figure is given. For the molecular weight and heterocyclic content, the extrapolation should not have a steep slope in any case. Sulfur values in wet filter cake and pyridine insolubles are from the Eschka method. Other results are by oxygen bomb combustions for oils or from oxidation by bromine or alkaline peroxide for aqueous samples.

V-F-3 Accounting for Products

Reactor products were collected in three vessels: the bulk of liquid in the tared stainless steel flask, a small amount of liquid condensate in the knockout vessel (obtained during gas collection), and gas in the rubberized fabric bag. During the first quarter hour of liquid sample collection, gas was vented to the air to purge the liquid sample flask of air. The gas sample was then collected for 45 minutes. The volumes are calculated on an hourly basis.

The initial accounting was made by adding the weights of the three samples. The weight of gas is the only complex measurement and is described below. The weights were:

	CU 48A1	CU 48A2
Liquid sample	977.1 g	953.7 g
Knockout vessel liquid	1.1 g	1.6 g
Gas sample	37.0 g	34.2 g
Total	1015.2 g	989.5 g
% Recovery of feed	98.5	97.8

The distribution of liquid product weights on a loss-free basis is an intermediate step in calculating yields (table 4). The grams of each product made from each sample are taken from these data and presented in tables 7 and 8 without the details of necessary corrections for handling losses and products taken as analytical subsamples.

V-F-4 Composition of Products

The weight of product gas is obtained by calculation from the gas analysis data and gas volume data. Product gas is reduced to an air-free basis on the assumption that any oxygen present is caused by incomplete flushing of the sample flask in the first 15 minutes of the sample period. It is also assumed that any air present replaces an equal volume of air-free gas, which remains in the liquid sample flask. The analytical methods are described in section IV-D-1. Water is measured by cold trap weight gain when the gas bag is vented; gas volume is measured by venting the bag through a wet test meter. Tables 9 and 10 summarize product gas composition.

Each of the materials reported in the summary tables, tables 7 and 8, was analyzed for carbon, hydrogen, nitrogen, and sulfur. The composition of vacuum bottoms is shown in table 11.

1. Water was determined in some samples, by Karl Fischer titration, and phenol by ultraviolet spectrophotometry. Traces of phenol in water (usually 3/4%) were neglected in the results computation since the contribution to the carbon balance is trivial. The ammonia and and sulfide figures are included.

2. Ash was determined in appropriate samples, though not in filtrates (usually 0.03 or 0.04% ash). The primary separation reported in tables 7 and 8 includes ash from the wet filter cake only.

Table 9. PRODUCT GAS COMPOSITION, CU 48A1[a]

SUBSTANCE	MOL. WT.	AIR-FREE VOLUME %	WEIGHT (g)	C (g)	H (g)	S (g)	O (g)
H_2	2.016	73.94	7.511		7.511		
CH_4	16.04	9.32	7.532	5.640	1.892		
C_2H_6	30.07	2.91	4.409	3.522	0.887		
C_3H_8	44.09	1.45	3.221	2.632	0.588		
C_4H_{10}	58.12	0.85	2.489	2.057	0.432		
CO	28.01	0.52	0.734	0.314			0.42
CO_2	44.01	1.68	3.726	1.016			2.71
H_2S	34.08	3.64	6.250		0.370	5.88	
H_2O[b]	18.02		(1.47)				
N_2[c]	28.02	(5.70)	(8.047)				
Total		100.01	35.87	15.14	11.68	5.88	3.13

[a] Hourly volume: 132.3 liters, measured by wet test meter at 25.5°C and 733.5 mm Hg. Corrected to dry gas at STP:

$$\frac{(132.3)(273.1)(733.5 - 24.5)}{(298.6)\ (760)\ (22.4)} = 5.039 \text{ moles}$$

[b] Obtained as gas is vented through cold trap and wet test meter; this water is included with knockout vessel water in balance.

[c] N_2 is from gage purge; not entered as input for material balance nor reported in gas output.

Table 10. PRODUCT GAS COMPOSITION, CU 48A2[a]

SUBSTANCE	MOL. WT.	AIR-FREE VOLUME %	WEIGHT (g)	C (g)	H (g)	S (g)	O (g)
H_2	2.016	77.70	8.719		8.719		
CH_4	16.04	6.46	5.767	4.318	1.448		
C_2H_6	30.07	2.32	3.882	3.101	0.781		
C_3H_8	44.09	0.97	2.380	1.944	0.436		
C_4H_{10}	58.12	0.62	2.006	1.656	0.350		
CO	28.01	0.40	0.624	0.267			0.36
CO_2	44.01	1.20	2.939	0.802			2.13
H_2S	34.08	3.09	5.861		0.357	5.504	
H_2O[b]	18.02		(2.000)				
N_2[c]	28.02	(7.19)	(11.209)				
Total		99.95	32.18	12.08	11.39	5.504	2.49

[a] Hourly volume: 146.4 liters, measured by wet test meter at 26.50°C and 736 mm Hg. Corrected to dry gas at STP:

$$\frac{(146.4)\ (736 - 26.0)\ (273.1)}{(760)\ (299.6)\ (22.4)} = 5.566 \text{ moles}$$

[b] Obtained as gas is vented through cold trap and wet test meter; this water is included with knock-out vessel water in balance.

[c] N_2 is from gage purge; not entered as input for material balance nor reported in gas output.

Table 11. CU 48 VACUUM BOTTOMS

MATERIAL	% IN CU 48A1	% IN CU 48A2
Carbon	87.50	87.32
Hydrogen	5.23	5.11
Nitrogen	2.040	1.909
Sulfur	0.882	0.944
Oxygen	4.17	4.58
Ash	0.179	0.133
	100.001	99.996

3. Cut 2 oil composition includes carbon from combustion and hydrogen from the IR correlation. Hydrogen from the combustion method will check the IR value within the precision of a single trial; but since IR correlation uses the average of many trials and can be reproduced with precision, it is considered more precise than the single combustion result. Combustion results are used for the hydrogen of all other products.

4. Sulfur was determined repeatedly in wet filter cake and pyridine insolubes by the oxygen bomb method in order to establish sulfur values presented. The insolubles must be diluted considerably with benzoic acid to insure combustion; the proportions are critical, and enough fuel to insure complete decomposition is required. The analyses are therefore duplicated by the Eschka method:

	% S (oxygen bomb)	% S (Eschka)
Wet filter cake		
CU 48A1	4.66	4.70
CU 48A2	4.772	5.14
Pyridine insolubles		
CU 48A1	8.128	8.680
CU 48A2	8.930	9.14

SECTION VI

REVIEW OF ELEMENTAL BALANCE CALCULATIONS

This section discusses both the reasons for failure to make an exact element-by-element balance and the gains made from the study. It includes alternate analyses, with some comment on the reporting system, to assist in interpreting and evaluating the results. Failure to make an exact elemental balance was caused by operating errors, practical difficulties in treating raw data, and, in one case, the limitations of available analytical techniques.

VI-A MATERIAL LOSSES

The chief practical difficulties in obtaining a material balance were caused by settling of mineral, holdup of sample material in collection vessels, and loss of water from feed coal.

VI-A-1 Ash

Mineral contains much of the sulfur to be reported. But raw samples did not contain as much ash as the feed slurry should have contained. Since the mineral balance must be closed to account for all sulfur, the ash balance was forced mathematically. Such an operation is normal to loss-free yield calculation; and because sulfur results for the individual samples were satisfactory, the data based on a forced ash balance do account for input sulfur very well.

The need for this forced balance arises from a fact frequently mentioned earlier: mineral in this process tends to settle in the feed vessel, in the dissolver, and in the sample flask, which results in preferential loss of ash and associated unreacted organic matter. The significance of this fact was better understood during CU 48 than the way to handle it. Since CU 48, the refinements in both mixing of feed slurry and ash suspension have permitted better reporting of ash input. For better reporting of ash output, several measures have been taken.

It will be noted that the primary and secondary separations in CU 48 both account for the same weight of ash. The loss could be the amount settled in the reactor tube or the amount clinging to the inside of the sample flask, probably the latter since the time allowed to line out the reactor should have been long enough to equilibrate the mineral bed settled in the dissolver. For CU 48, the liquid sample flasks had been cleaned. After stripping, each was emptied into a filter. Material held up on the sides of the flask, and lost from the sample for further analysis, was 14 g for CU 48A1 and 12.5 g for CU 48A2, or more than 1%. Because the holdup is richer in mineral than the material filtered, and because ash is about 8% sulfur, prorating lost material to the liquid product distribution for loss free calculation will build in some error.

The more recent practice permits better reporting. In later work, the same coal and a recycled solvent make up the slurry for long series of runs; sample material tends toward uniform viscosity; larger samples improve recovery percentages; and the holdup in sample flasks is not cleaned out between runs so that net holdup on successive uses is negligible. Material accounting is within 1/4% at this stage of workup.

The precise accounting for materials also suggests a long sample interval to account for ash. The 1-hour samples taken during CU 48 might better have been a single 40-hour sample for two reasons. First, lineout would have been assured. Second, the long collection would tend to overcome the effect of mineral variation found in the samples taken more frequently. (The characteristic of the upflow reactor to discharge mineral contents in cycles is described in section III; its effect on blackness and $\overline{IR}$ measurements is indicated in appendix J, representing 20 successive 4-hour samples in a later experiment.)

To allow for the loss of ash, CU 48 material balances were forced by calculation of weights of insoluble material and wet filter cake, from weight of input ash, analysis of wet filter cake, and composition of pyridine-washed insolubles from the filter cake. The holdup of material in sample flasks or water vapor in the gas collection bag is a small percentage, but it forces a prorating of the elemental constituents to the product distribution in loss-free accounting.

VI-A-2 Water

Feed coal was sampled and subjected to ovendrying and also Karl Fischer titration for water at the time the coal was initially ground and when the sublot was taken for use in CU 48. A later check of water in a retained sample of the coal gave 3.25% by the titration and 2.0% by ovendrying. Assuming the input solvent contained no water, after its stripping to 50°C at 3 mm Hg, the slurry evidently had up to 1.08% water at the 2:1 solvent:coal ratio.

Feed slurry was analyzed by Karl Fischer titration for water; the results were too high. Feed coal could not account for water indicated by titration of slurry. Feed slurry was operated warm (60-70°C), probably causing preferential loss of some water and the lightest fraction of solvent, perhaps 1% of slurry weight. Since the feed vessel was on a scale and total weight was charged to slurry fed, the weight of water and oil evaporated was recorded as material fed. The effect on mass balance and oxygen balance is discussed with the recalculations later.

The output water is mostly cold-trapped. The collective weight is determined by weighing water from several trapping operations. The efficiency of these traps therefore influences the accuracy of the oxygen balance. As a check on the procedure, an additional cold trap has occasionally been used to collect any vapor overflow from the trap collecting water and cold trap oil at stripping. It may collect an additional 5-10%; thus, the error in collecting light materials may permit an increase of 1-2 g water and 0.5 g oil in the samples. Holdup of moisture in the gas collection bag can only be estimated. It can be concluded, however, that the uncertainty of the oxygen by difference is large enough to create larger average errors than the loss by cold trap overflow or inefficiency and other verifiable losses.

VI-B RECALCULATIONS

The elemental balances for CU 48A1 and CU 48A2 were recalculated several times. The first trial balances are shown in appendixes K and L. The first trial used the analysis of that lot of feed coal from the averaged sample taken at the time the coal was ground, with results of Karl Fischer titration for water in the feed slurry for the estimate of water input. After the check on the retained sample of feed coal and the discovery that the coal could not account for water indicated by slurry titration, the composition of the feed slurry was reviewed. It was assumed that the only water present was that in the coal. An oxygen balance was calculated, by difference for all samples, from the results of the best available elemental analyses. This balance indicated more oxygen in the feed than in the products. Since the warmed feed vessel had actually lost water to evaporation during recirculation in the feed loop, a second trial balance was attempted.

The second trial assumed the coal to contain 3.25% moisture as weighed, and also assumed the slurry to have lost this water by the time slurry entered the reactor. This procedure does result in the best accounting for oxygen, although complete loss of water is unlikely. The probable failures of Karl Fischer titrations to determine the facts leaves no numerical value for water in the slurry. Qualitatively, the value would best be approximated between 0.00% for a dry sample, and 1.08%, which would represent the slurry resulting from a 2:1 blending of moisture-free solvent with coal with 3.25% water.

Since total loss of water from the feed vessel would increase the weight of organic matter fed about 1%, the high final C and H yields become reasonable. For inputs considered, the 1% is 10.2 g H_2O or 9.1 g O_2. If this oxygen is used to correct the oxygen balance, nearly all material is accounted for. Incomplete recovery of water from the gas bag, cold traps, condenser, etc. is the probable cause for residual error.

The summary tables, tables 7 and 8, show that carbon and hydrogen are accounted for within a percentage or so. The correction to 100% recovery of feed required the addition of 1.5% and 2.2% of material prorated to product liquid distribution in the two balances. This practice is suspect wherever material lost is not representative of material retained for analysis.

VI-B-1 The Reporting of Sulfur

The elemental balance study, then, enforced a full review of sampling techniques. In addition, the effort to confirm balances by alternative and duplicate analyses has revealed limitations in the available methods, which suggest separate causes for imprecise results.

For sulfur, the difficulty of decomposing mineral-rich samples (wet filter cake and pyridine insolubles) by standard ASTM oxygen bomb methods has been mentioned. Results by the Eschka method have been compared. Table 12 shows the higher results obtained in CU 48 by the second method.

VI-B-2 The Reporting of Nitrogen

The determinations of carbon, hydrogen, and sulfur were satisfactory or good. This is not true for nitrogen.

Table 12. COMPARATIVE SULFUR ANALYSES (%)

MATERIAL	OXYGEN BOMB		ESCHKA	
	CU 48A1	CU 48A2	CU 48A1	CU 48A2
Coal (dry basis)	4.94	4.94		
Solvent	0.36	0.36		
Knockout H_2O	0.547[a]	1.25[a]		
Cold trap H_2O	0.821[a]	0.841[a]		
Cold trap oil	0.65	0.886		
Filtrate	0.45	0.46		
Cut 1 oil	0.20	0.244		
Cut 2 oil	0.40	0.377		
Heavy oil	0.815	0.842		
Vacuum bottoms	0.882	0.944		
Wet filter cake	4.66	4.772	4.70	5.14
Pyridine insolubles	8.128	8.930	8.680	9.14

a No decomposition necessary; treated with bromine water and gravimetric finish

For coal, solids, and materials of high molecular weight, the reliability of nitrogen determinations has been a question for some time. The Kjeldahl method is often regarded in Germany as inaccurate for coal.[1]

> The Kjeldahl or Dumas method is generally used for the determination of nitrogen in solid fuels. There appears to be a considerable difference of opinion among fuel analysts as to which method gives the most reliable results . . . . Bunte and Schilling applied the Kjeldahl method to the analysis of solid fuels shortly after it was published and found it yielded very consistent results . . . [yet] The values obtained by the Kjeldahl and Dumas methods (the latter including a subsequent combustion with oxygen) may differ by as much as 46% for coal.[2]

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[1] W. M. Ode. "Coal Analysis and Mineral Matter." The Chemistry of Coal Utilization, ed. H. H. Lowry. (New York: J. H. Wiley, 1963). P. 214.

[2] W. R. Kirner. "Microchemical Analysis of Solid Fuels." Industrial and Engineering Chemistry. Vol. 7, No. 5 (July, 1935). P. 296.

The reasons for this difference, already indicated by the present study, are primarily that Kjeldahl does not report enough of the nitrogen actually present, however reproducible Kjeldahl analyses may be.

In preparation for the elemental balance study here, a technique study with various standard catalyst systems and various digestion times had been made. Obtaining the same result from trial to trial presented little or no problem; the results obtained were repeated with great precision, and with standard Kjeldahl reagents and different digestion times. An example for coal is illustrated in table 13. With such consistency in Kjeldahl analytical results, it was naturally disturbing later on to demonstrate an excess of nitrogen out of the reactor over that amount put in. (The first trial balances, appendixes K and L, show 114% and 113% nitrogen recovery.)

The initial sample set for the elemental balance study was analyzed for nitrogen by Kjeldahl, with mercury and selenium to catalyze the digestion. None of the modifications of the method seems to produce significantly higher nitrogen results than the ASTM method. To confirm initial results, the samples of all significant products were analyzed by the Dumas method in the Schwarzkopf Microanalytical Laboratory. The results, table 14, for replicate Dumas analyses give values from 1.25% to 1.64% in feed coal. Because of the laboratory location, it was not possible to search for systematic errors in the measurement; but these results are not considered suspect. Results with the Coleman automatic Dumas nitrogen analyzer have followed the pattern also: Dumas results are always higher than Kjeldahl.

Table 13. REPRODUCIBILITY IN FEED COAL NITROGEN RESULTS (KJELDAHL)

SAMPLE WEIGHT (g)	ml H_2SO_4 (0.10034)	% N^b	DEVIATION		$\sqrt{\frac{\Sigma d^2}{n-1}}$
			d	d^2	
Set 1^a					
1.0373	10.30	1.369	+0.022	0.00048	
1.0235	9.90	1.332	-0.015	0.00023	
1.0572	10.55	1.376	+0.019	0.00036	1.347±0.03
1.0245	10.12	1.361	+0.014	0.00020	
1.0908	10.25	1.295	-0.052	0.00270	
Blank	0.20	(1.347) average			
Set 2^a					
1.0722	10.35	1.350	-0.011	1.21×10^{-4}	
1.0341	10.10	1.366	+0.0005	2.5×10^{-7}	
1.0083	6.55	0.806 lost			1.366±0.0064
1.0673	10.40	1.363	+0.0002	0.8×10^{-3}	
1.0453	10.20	1.365	+0.004	1.6×10^{-7}	
Blank	0.05	(1.366) average			
Set 3^a					
1.0040	9.80	1.358	+0.006	3.6×10^{-5}	
1.0108	9.75	1.342	-0.010	1×10^{-4}	
1.0064	9.75	1.348	-0.004	1.6×10^{-5}	1.352±0.0512
1.0687	10.15	1.322	-0.030	0.9×10^{-3}	
1.0499	10.48	1.390	+0.038	1.488×10^{-3}	
Blank	0.60	(1.352) average			

[a] Samples in set 1 were allowed 2 hours digestion after the green color appeared; set 2 allowed 3 hours; and set 3 allowed 4 hours. Regents were 0.7 g mercuric oxide (red) selenium and kelpack plus 30 g H_2SO_4 (concentrated).

[b] The same coal was analyzed by the Dumas method in various milligram sample sizes, with these results:

42.780 mg	1.09 %N
33.930 mg	1.11 %N
24.830 mg	1.30 %N
23.080 mg	1.21 %N
13.220 mg	1.58 %N
13.138 mg	1.58 %N

Table 14. ALTERNATE NITROGEN DETERMINATIONS

	CU 48A1[a]		CU 48A2[a]	
SAMPLE	SAMPLE SIZE (mg)	%N	SAMPLE SIZE (mg)	%N
Feed coal	40.345	1.25		
	34.828	1.30		
	30.460	1.37	(Same Coal)	
	20.290	1.39		
	13.461	1.64		
	13.772	1.51		
Cut 1 Oil	25.110	0.67	30.315	0.58
	21.100	0.68	26.643	0.61
	15.100	0.65	21.869	0.63
	11.005	0.66	16.790	0.55
	C 7.878	0.54	C 14.563	0.55
	C 7.706	0.54	C 8.015	0.53
	C 4.704	0.59	C 5.039	0.54
Cut 2 Oil	24.928	1.06	22.792	0.84
	18.440	0.99	16.820	0.80
	13.665	1.01	12.570	0.91
	C 11.858	0.76	C 11.201	0.75
	C 10.451	0.76	C 10.782	0.74
	9.427	1.14	8.310	0.77
	C 6.760	0.81	C 5.340	0.76
Filtrate	25.810	1.03	24.580	1.06
	21.760	1.01	19.492	1.11
	14.120	1.05	14.610	1.03
	9.390	1.15	9.820	1.19
Heavy Oil	20.645	1.54	17.580	1.56
	16.060	1.63	12.115	1.69
	12.035	1.70	9.343	1.77
	8.510	1.75	7.705	1.78
Vacuum bottoms	21.855	1.84	20.551	1.91
	17.812	1.86	16.370	1.97
	12.365	2.13	11.553	2.17
	8.885	2.03	8.740	2.20
Wet filter cake	26.834	0.905	24.565	0.994
	19.828	0.978	19.510	1.07
	14.611	1.02	15.070	1.03
	10.585	1.04	8.840	1.12
Pyridine insolubles	39.330	0.701	40.452	0.704
	31.710	0.724	30.665	0.663
	20.062	0.734	22.048	0.800
	15.180	0.756	16.048	0.783

[a] All determinations were by Dumas except as noted: C indicates colorimetric determination. Analyses were made between 23 and 25°C at 760-778 mm Hg, at Schwarzkopf Microanalytical Laboratory.

As an added refinement in the search for an explanation, the practice was to run several Dumas samples of different sizes and then to extrapolate to zero size, on the theory that larger samples deposit larger amounts of coke residues containing nitrogen. If nitrogen values in table 14 for duplicate analyses of each sample are plotted by sample size, the values may fall on a straight line or scatter or form an array forcing an arbitrary choice between extrapolation or calculated average, to afford the probable nitrogen content in the product. The Dumas extrapolation for feed coal (table 15) materially increases the nitrogen estimate. If an elemental balance is made with this result and with the Kjeldahl analyses of products, the nitrogen input substantially exceeds the nitrogen output.

This condition is partially correctable by using the extrapolated Dumas method for all input materials and for all product samples; the final balance then indicates some loss of nitrogen in workup or collection of materials. This situation is more reasonable than the original, in which nitrogen in the products exceeds nitrogen input. But extrapolation of the Dumas results to zero sample size is at best a dubious procedure. There appears no particular reason to suppose that the result is accurate.

Apart from conscientious applicaton of established methods, it was considered that nitrogen by difference in liquid products and ash-free solids might be determined if an accurate oxygen analysis were available. Since the carbon and hydrogen analyses are sufficiently accurate for tracing these elements, and since judicious use of oxygen

Table 15. COMPARATIVE NITROGEN ANALYSES (%)

MATERIAL	KJELDAHL		EXTRAPOLATED DUMAS		OTHER	
	CU 48A1	CU 48A2	CU 48A1	CU 48A2	CU 48A1	CU 48A2
Coal (dry basis)	1.30		1.85			
Solvent	0.60		1.07-1.11		0.77[b]	
Knockout H_2O					0.24[c]	0.55[c]
Cold trap H_2O	0.38[a]	0.485			0.38[a]	0.485[a]
Cold trap oil	0.212	0.219				
Filtrate	0.981	0.979	1.17	1.28		
Cut 1 oil	0.566	0.560	0.665	0.69-0.74	0.56[b]	0.54[b]
Cut 2 oil	0.765	0.734	1.14-1.19	0.91-1.00	0.74[b]	0.75[b]
Heavy oil	1.611	1.627	1.87	1.92		
Vacuum bottoms	2.04	1.909	2.20	2.27		
Wet filter cake	0.895	0.868	1.08-1.10	1.10		
Pyridine insolubles	0.644	0.590	0.775	0.90		

a Ammonia in H_2O phase, distilled over MgO

b Colorimetric N (Schwarzkopf)

c H_2O in the knockout vessel was used up by the analysis for sulfur (as NH_4SH), from which N values are taken.

bomb and Eschka decompositions give accurate sulfur results, only oxygen or nitrogen must be measured precisely; the other is then determined by difference. Thus, the conventional nitrogen analysis might be checked by the neutron activation analysis for oxygen. Unfortunately, the method would have limited use; neutron activation is difficult to apply in substances with mineral because the oxygen in mineral is also determined along with oxygen in the non-mineral material, and prorating oxygen to the separately reported ash would be artful. Therefore, a method for the simultaneous analysis of ash from the coal and analysis of the coal sample would be desirable. It was concluded from these investigations that separate determinations are preferable, since any result obtained by difference will sum the errors in all determinations involved. The manipulations that gave an oxygen balance were justified only by achieving carbon, hydrogen, and sulfur balances in the data sets; yet the accuracy of the oxygen balance could be affected materially by the accuracy of the nitrogen balance.

Neither functional group analysis nor IR spectroscopy accounts for all nitrogen or oxygen in a dependable way. Analyses for the light fractions are better than for high molecular weight fractions. For coal, the information from functional group determinations generally supports the conversion of part of the nitrogen to amine functions, with hindered or neutral functions accounting for an appreciable fraction of the total nitrogen in the higher molecular weight materials. Application of the Kjeldahl method to the higher molecular weight fractions is thus subject to increasing risk of error, while coal itself appears to be the material most prone to cause difficulty. In general, the use of the Dumas method has failed to produce precise results; methods for correction of the Dumas method are also a question.

Input solvent and reclaim solvent cuts have been routinely analyzed by infrared spectroscopy. In these materials absorption bands are found at the usual locations for OH (phenolic) and NH_2 (amine) functions. (The spectra for oils and coal solution are shown in appendixes E through I.) These materials have also been titrated by conventional nonaqueous procedures which determine even weakly basic functional groups and weakly acidic functional groups, such as hindered phenols.

When basic material is determined by titration, the result can be related to the nitrogen present in the sample. For low boiling products from the SRC process, the basic nitrogen function accounts for most of the nitrogen reported by the Kjeldahl method. As molecular weight increases, the fraction of the total nitrogen accounted for by titration of basic functional groups declines. For cut 2 reclaim solvent, this may account for only 30 to 50% of the total nitrogen present. Efforts to titrate vacuum bottoms in mixtures of tetralin and acetic acid resulted in similar estimates for the proportion of the nitrogen as basic functions in this material. The latter results may involve solubility problems and are perhaps less accurate.

In lower boiling fractions the determination of acidic functions by titration gives results in which the oxygen as phenolic functions and oxygen-by-difference were similar. As higher molecular weight products are studied, this result also fails to account for the oxygen completely. The location of inflection points, as in the titration of vacuum bottoms dissolved in pyridine, becomes difficult. Problems with solubility and perhaps with hindrance of functional groups may be involved.

Evidently another method should be used to check the results or to replace the Dumas extrapolation method. Of established methods, probably the only remaining is gasification, reported in the article by W. M. Ode just noted, as an alternative determination for nitrogen in coal. Ode refers to *Deutscher Normenauschuss*, DIN 51722. The detailed method is not readily available; it is given in brief form in English by Ode and also in brief form in German elsewhere.[3] From these two sources, it appears that the decomposition of 0.5-1.0 g coal for quantitative yields of contained nitrogen in ammonia is practical. Application of the gasification method to SRC products would entail additional studies. Its application to the more volatile materials could be troublesome; so the Kjeldahl method here seems reasonable.

At the present time, therefore, the selection of best analytical methods and reporting systems for nitrogen in the heavier materials of the SRC process is, at the least, in need of further study.

VI-C GAINS FROM THE STUDY

After the elemental balance study, several facts emerged. First, the performance of the continuous reactor could be improved. To improve uniformity in slurry actually fed, a campaign of mechanical corrections and control analysis was conducted. Sample collection and workup procedures were both optimized, especially by collecting samples over longer intervals and learning to work up these larger samples. As a result, raw material balances usually close at better than 99% recovery, often better than 99.5%.

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[3] W. Radmacher. "Brennstoffe, feste, flüssige." *Ullmans Encyklopädie der technischen Chemie*, dritte auflage. (München: Urban und Schwarzenberg, 1953). Band 4, P. 701.

Second, a better control of coal sampling and preparation was needed. The considerable attention given has greatly reduced the risk of segregation or nonuniformity of coal lots from can to can. Long experiments are now made with slurry composition under good control.

Third, the fate of sulfur and nitrogen in the SRC process seems clarified. As yet, the interdependence of solvent composition, solvent reactivity, coal composition, operating conditions, and equipment design is not fully elucidated. But an appreciable part of the sulfur in the vacuum bottoms fraction, the large source of fuel value recovered, can be removed. Removing an appreciable fraction of the nitrogen seems improbable, perhaps requiring liquefaction under conditions that convert all material to hydrocarbons of appreciably lower molecular weight than is usual now in the SRC process.

In addition, certain assessments of reactor behavior and analytical methods have been assisted by the elemental balance study. The problem of mineral behavior was not solved by mechanical corrections. When mineral output has been measured frequently as a function of time, its concentration in the effluent product has always varied in a cyclic manner. For the upflow type of dissolver being studied, this seems a normal characteristic; the effect of scaleup is not known, but mineral behavior may be influenced by initial particle size of the coal or by such mineralogical factors as the dispersal of crystallite sizes in the coal minerals. It further appears that to collect a set of samples for an exact element-by-element balance will require good understanding of the operating characteristics of the larger dissolver and its auxiliary equipment items.

GLOSSARY

aromatic - liquid aromatic hydrocarbons in solvent or derived from the reaction with coal; substituted benzenes, indenes, naphthalenes, acenaphthylenes, phenanthrenes, anthracenes. The term includes phenols, anilines, quinolenes, and pyridines.

ASTM - American Society of Testing Materials

blackness - determination of visible absorbance; applied to coal solutions as an empirical measure of the coal which is in solution

cm - centimeter(s)

coal converted - the amount of coal changed to gaseous, liquid, and solid products. The percentage is determined from pyridine insolubles data, by either of two methods:

A. Insolubles Difference Method

% feed coal converted = 100 - % pyridine insolubles, loss free basis in reference to feed coal

B. Ash Enrichment Method

100 (% ash in feed coal)=(100 - X) (% ash in pyridine insolubles)

where X is % feed coal converted

Both methods are subject to some error. The first depends on quantitative collection of unreacted material; if handling losses are corrected for in the calculation, materials lost must contain the proper ratio of liquids and solids, which is rarely the case. The second method requires that mineral and carbonaceous material, not dissolved, remain in the proper ratio; settling at any point may segregate mineral preferentially, and this will cause error. The true percentage of coal converted probably lies between results by the two methods.

Since different coals may have different moisture and ash contents, it is often desirable to reduce conversion to the moisture-ash-free (MAF) basis, representing the organic fraction of the coal:

$$\%\ \text{MAF conversion} = \frac{(\%\ \text{conversion on feed coal basis})(100)}{100 - (\%\ \text{ash} + \%\ \text{moisture})}$$

cold trap oil - During vacuum stripping of the reaction product, liquids are collected in a cold trap cooled with dry ice and acetone. After thawing, a two-phase product is obtained. The upper phase is a hydrocarbon mixture consisting of materials with an atmospheric pressure boiling range from approximately 20-175°C with a density of approximately 0.80. It is a mixture of aliphatic and naphthenic hydrocarbons, essentially a stabilized naphtha. The lower phase is mostly water.

cut 1 oil - a distillate obtained during stripping of the reaction product in recent work (100°C at less than 3 mm Hg); during CU 48 it was obtained as the 50-100° ≤3 mm Hg cut after filtration; boiling range approximately 175-288°C at atmospheric pressure, density 0.9-1.0. In the Pilot Plant this cut will be used to wash the filter cake; any excess may be used as solvent or disposed of as product.

cut 2 oil - the vacuum distilled filtrate (100-230°C at ≤3 mm Hg) reclaimed for solvent; at atmospheric pressure, the boiling range is 288-425°C; density of 1.1 if derived from anthracene oil. Cut points may be adjusted to obtain breakeven quantity for continuous operation of the reactor.

g - gram (s)

heavy oil - any distillate boiling above 230°C to the end point (maximum 325°C) at ≤3 mm Hg. The theoretical distillation range at atmospheric pressure may be 425-560°C; density is near 1.2. This oil is viscous and may be solid at 20°C; it may not be isolated in the continuous plant (the cut 2 end point may be raised to utilize a fraction as solvent, leaving the rest in the vacuum bottoms).

hydroaromatic liquid - typical compounds are reaction products of aromatic liquids and hydrogen: indenes, dihydronaphthalenes, tetralin, dihydrophenanthrenes, tetrahydrophenanthrene, dihyroquinoline. Normally this term implies a partly hydrogenated aromatic compound.

IR - infrared

$\overline{\text{IR}}$ - infrared ratio (section IV-D-2-d); absorbance at 2920 cm^{-1}/absorbance at 3040 cm^{-1}

kg/cm^{2} - kilogram(s) per square centimeter

l - liter(s)

light liquids - see "cold trap oil"

LHSV - liquid hourly space velocity (section IV-A-3)

m - meter(s)

MFRAO - middle fraction, raw anthracene oil

meq/min. - milliequivalents per minute (appendix D)

mg - milligram(s)

ml - milliliter(s)

mv - millivolt(s)

MAF - moisture and ash free

OCR - Office of Coal Research

ppt - parts per thousand

polymer - a compound of high molecular weight, derived either by the addition or condensation of many smaller molecules. In this context coal is a polymeric condensation product with a wide variety of monomeric units. For this study, polymer may result from interaction of solvent and coal derived fragments to product higher molecular weight, less soluble materials. This production is induced by high temperatures or too low partial pressures of hydrogen.

pyridine insolubles - the residue of unconverted carbonaceous material (insoluble organic matter) and mineral matter from feed coal, which results from treating filter cake. To determine the amount of coal converted, the wet filter cake must be washed free of imbibed coal solution (or residual wash oil, if applicable). A weighed portion of filter cake is digested in hot pyridine, filtered, washed with hot pyridine until washings come through colorless, rinsed sequentially with benzene and acetone to remove pyridine, and then dried and weighed. See "coal converted."

R&D - Research and Development

saturates - typical compounds are cyclohexane, decalin, and aliphatic hydrocarbons from ring openings or side chain removals

SRC - Solvent Refined Coal; vacuum bottoms

SHMFRAO - stripped hydrogenated middle fraction, raw anthracene oil

vacuum bottoms - end product after solvent extraction, the residue from vacuum distillation of filtered coal solution. It is actually the high molecular weight fraction of the coal dissolved in the process.

water phases - water collected in the cold trap with light liquids, or collected with cut 1 oil and combined to obtain a consolidated value simulating total water yield from the coal process. Water originates as water fed with the coal or produced by the reaction of hydrogen with oxygen-containing functions in the coal. Water phases may contain variable amounts of ammonia, carbonate, sulfide, phenol, or other water soluble organic compounds available for extraction. A small amount of water also collects in the knockout vessel and is cold-trapped in the gas collection bag as gas is vented and sampled.

wet filter cake - the insoluble materials retained on the filter as a cake of solids after filtration of the stripped coal solution, containing 40-60% imbibed solution

APPENDIX A

THE PITTSBURG & MIDWAY COAL MINING COMPANY
RESEARCH DEPARTMENT
Analytical Laboratory

DETERMINATION OF HYDROGEN SULFIDE IN SRC PRODUCT GAS

Data: This method covers the determination of hydrogen sulfide in product gas from SRC lab unit. It is applicable on a concentration range of about 0.1 to 7% V/V H_2S. A measured volume of product gas is bubbled through ammoniacal zinc sulfate solution to remove hydrogen sulfide. The amount of hydrogen sulfide in the absorber is then determined iodometrically.

Special Apparatus:

(a) A 250 ml Erlenmeyer flask with a two-hole rubber stopper carrying (1) a 7-mm diameter glass tube, with a drawn down tip, extending nearly to the bottom of the flask and (2) a short 7-mm diameter glass tube, extending just a short distance on either end of stopper, for exit of excess unabsorbed gas. On the inlet end of the (1) inlet-tube, a 1-ft long rubber injection tube is attached. On the outer end of the (2) exit tube, a small rubber bulb having a small slit cut in it can be used as a 'flap' valve to restrict the rapid flow of gas and to exclude the entrance of air.

(b) Gas Syringes, 500 or 1000 ml - Hamilton Super Syringes No. S-0500 or S-1000.

Reagent Solutions:

(a) Ammoniacal Zinc Sulfate. Dissolve 50 grams of zinc sulfate heptahydrate in 250 ml of water, and then slowly add 250 ml of concentrated ammonium hydroxide while stirring. Filter off any precipitate that may form upon long standing.

(b) Hydrochloric Acid 1;1. Dilute concentrated HCl with an equal volume of water.

(c) Iodine Solution (0.05N) - Weigh 12.8 g of resublimed iodine crystals into a 250 ml beaker. Add 40 g of potassium iodide (KI) and 100 ml of water. Stir until solution is complete, dilute to 2000 ml, mix thoroughly, and store in a brown-glass reagent bottle. (No need to know iodine solution normality exactly if it does not change and the same exact amount volume (25.0ml) is used in reagent blank and sample determinations).

(d) Sodium Thiosulfate Standard Solution (0.05N) - Dissolve 25 g of sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$) in 500 ml water and add 0.01 g sodium carbonate (Na_2CO_3) to stabilize the solution. Dilute to 2000 ml and mix thoroughly. Standardize verus potassium dichromate or potassium iodate by usual techniques to accuracy of ± 2 ppt.

(e) Starch Solution, 2%. To 250 ml of boiling water, add a cold suspension of 5 g of soluble starch and 0.025 g mercuric iodide. Boil for a few minutes to clear. Store in glass-stoppered bottle with undissolved mercuric iodide on bottom.

Sampling

The product gas must be analyzed for H_2S as soon as possible after receipt. Hydrogen sulfide can react with any condensed water vapor or ammonia and can come out of the gas mixture. It may also dissolve in the sides of the bag and be lost. The effect of it possibly combining with carbon monoxide to form carbonyl sulfide (COS) is not known. It would be preferred if the gas could be sampled at the source.

Procedure:

Transfer 30 ml, by graduate, of the ammoniacal zinc sulfate solution to a 250 ml Erlenmeyer flask. Dilute with water to about 150 ml and add a 1-1/2 inch stirring bar. Put in inlet tube-valved stopper. Attach filled gas syringe to injection tube by means of a short piece of glass or stainless steel tubing. While magnetically stirring, slowly inject 100 ml to 1000 ml of product gas depending on H_2S percentage. (Watch for heavy turbidity formation as guide to the volume of gas to use in first test.) (Caution: This part of test should be done in area free of open flames or sparks. Also if gas contains much carbon monoxide, it should be done in good fume hood!)

Remove syringe from injection tube and record volume of gas injected into flask. Raise rubber stopper just enough to bring end of inlet tube out of solution and wash down the injection tube with about 1 ml of 1:1 HCl and a little water from a wash bottle. Transfer the stirring bar, by means of a thief, from the 250 ml E flask to a 500 ml Erlenmeyer flask containing 25.0 ml of 0.05N iodine solution (by pipet) and 40 ml 1:1 HCl solution (by graduate). While stirring continuously, very slowly pour the contents of the absorbing 250 ml flask into the 500 ml E flask. Rinse the 250 ml flask with about 100 ml water into the 500 ml flask.

As quickly as possible, titrate the solution, while being stirred, with standardized 0.05N sodium thiosulfate solution until the solution is yellow. Then add 2 ml of 2% starch solution and continue titration to a permanent colorless end point. Record volume of sodium thiosulfate required for titration. Sample solutions are usually turbid at end of titration, blanks are clear.

Run through above procedure, leaving out gas sample, for reagent blank. The nature of this test is that the blanks are equal to or usually higher than the titration volumes obtained for samples.

The blank and sample tests should be run in duplicate. The blank values do not change very much, therefore only a weekly check is necessary if there have not been any changes in reagents, room temperature, etc. If sample titration volume is less than half of the reagent blank, test should be rerun using less gas sample.

Calculations:

$$\frac{(V_b - V_s) \times N_t \times F \times 100}{V\ gas} = \%H_2S\ (mole\ \%)$$

Where:

V_b = Volume (ml) of sodium thiosulfate used in blank

V_s = Volume (ml) of sodium thiosulfate used in sample

N_t = Normality of sodium thiosulfate

V gas = Volume (ml) of product gas used in test

F = Factor in milliliters of hydrogen sulfide per milliequivalent of sodium thiosulfate. It is one half of the reciprocal of the molar equivalent of one liter of gas (moles/liter) at temperature and pressure of product gas at time of testing. See "Molar equivalent of one liter of gas at various temperatures and pressures" table for ease of calculations. An average value of 12.5 can be used in the Kansas City Area.

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MOLAR EQUIVALENT OF ONE LITER OF GAS AT VARIOUS TEMPERATURES AND PRESSURES

Values in this table give the number of moles in one liter of gas. Values are based on the property of an "ideal" gas, calculated by use of the formula:

$$\text{moles/liter} = \frac{P}{760} \times \frac{273}{T} \times \frac{1}{22.40}$$

where P is the pressure in millimeters of mercury and T is the temperature in degrees Absolute (= °C + 273).

Pressure mm of mercury	Temperature °C											
	10°	12°	14°	16°	18°	20°	22°	24°	26°	28°	30°	32°
655	0.03712	0.03686	0.03660	0.03634	0.03610	0.03585	0.03561	0.03537	0.03515	0.03490	0.03467	0.03444
660	3731	3714	3688	3662	3637	3612	3588	3564	3541	3516	3493	3470
665	3768	3742	3716	3690	3665	3640	3614	3591	3568	3543	3520	3496
670	3796	3770	3744	3718	3692	3667	3642	3618	3595	3569	3546	3523
675	3825	3798	3772	3745	3720	3695	3669	3645	3622	3596	3572	3549
680	0.03853	0.03826	0.03800	0.03773	0.03747	0.03694	0.03697	0.03672	0.03649	0.03623	0.03599	0.03575
685	3881	3854	3827	3801	3775	3749	3724	3699	3676	3649	3625	3602
690	3910	3882	3855	3829	3802	3776	3751	3726	3702	3676	3652	3628
695	3938	3910	3883	3856	3830	3804	3778	3753	3729	3703	3678	3654
700	3967	3939	3911	3884	3858	3831	3805	3780	3756	3729	3705	3680
702	0.03978	0.03950	0.03922	0.03895	0.03869	0.03842	0.03816	0.03790	0.03767	0.03740	0.03715	0.03691
704	3989	3961	3934	3906	3880	3853	3827	3801	3777	3750	3726	3701
706	4000	3972	3945	3917	3891	3864	3838	3812	3788	3761	3736	3712
708	4012	3984	3956	3929	3902	3875	3849	3823	3799	3772	3747	3722
710	4023	3995	3967	3940	3913	3886	3860	3834	3810	3783	3758	3733
712	0.04035	0.04006	0.03978	0.03951	0.03924	0.03897	0.03870	0.03844	0.03820	0.03793	0.03768	0.03744
714	4046	4018	3989	3962	3935	3908	3881	3855	3831	3804	3779	3754
716	4057	4029	4001	3973	3946	3919	3892	3866	3842	3815	3789	3765
718	4068	4040	4012	3984	3957	3930	3902	3877	3853	3825	3800	3775
720	4080	4051	4023	3995	3968	3941	3914	3888	3863	3836	3811	3786
722	0.04091	0.04063	0.04034	0.04006	0.03979	0.03952	0.03925	0.03898	0.03874	0.03847	0.03821	0.03796
724	4103	4074	4045	4017	3990	3963	3936	3909	3885	3857	3832	3807
726	4114	4085	4057	4028	4001	3973	3947	3920	3896	3868	3842	3817
728	4125	4096	4068	4040	4012	3984	3957	3931	3906	3878	3853	3828
730	4136	4108	4079	4051	4023	3996	3968	3941	3917	3889	3863	3838
732	0.04148	0.04119	0.04090	0.04062	0.04034	0.04005	0.03979	0.03952	0.03928	0.03900	0.03874	0.03849
734	4159	4130	4101	4073	4045	4017	3990	3963	3938	3910	3885	3859
736	4171	4141	4112	4084	4056	4028	4001	3974	3949	3921	3895	3870
738	4182	4153	4124	4095	4067	4039	4012	3985	3960	3932	3906	3880
740	4193	4164	4135	4106	4078	4050	4023	3995	3971	3942	3916	3891
742	0.04204	0.04175	0.04146	0.04117	0.04089	0.04061	0.04033	0.04006	0.03981	0.03953	0.03927	0.03901
744	4216	4186	4157	4128	4100	4072	4044	4017	3992	3964	3938	3912
746	4227	4198	4168	4139	4111	4083	4055	4028	4003	3974	3948	3922
748	4239	4209	4179	4151	4122	4094	4066	4039	4014	3985	3959	3933
750	4250	4220	4191	4162	4133	4105	4077	4049	4024	3996	3969	3943
752	0.04261	0.04231	0.04202	0.04173	0.04144	0.04116	0.04088	0.04060	0.04035	0.04006	0.03980	0.03954
754	4273	4243	4213	4184	4155	4127	4099	4071	4046	4017	3991	3964
756	4284	4254	4224	4195	4166	4138	4110	4082	4056	4028	4001	3975
758	4295	4265	4235	4206	4177	4149	4121	4093	4067	4038	4012	3985
760	4307	4276	4247	4217	4188	4160	4131	4103	4078	4049	4022	3996
762	0.04318	0.04287	0.04258	0.04228	0.04199	0.04171	0.04142	4114	4089	4060	4033	4006
764	4329	4299	4269	4239	4210	4182	4153	4125	4099	4070	4043	4017
766	4341	4310	4280	4250	4221	4192	4164	4136	4110	4081	4054	4027
768	4352	4321	4291	4262	4232	4203	4175	4147	4121	4092	4065	4038
770	4363	4333	4302	4273	4243	4214	4186	4158	4132	4102	4075	4048
772	0.04375	0.04344	0.04314	0.04284	0.04254	0.04225	0.04197	0.04168	0.04142	0.04113	0.04086	0.04059
774	4386	4355	4325	4295	4265	4236	4207	4179	4153	4124	4096	4070
776	4397	4366	4336	4306	4276	4247	4218	4190	4164	4134	4107	4080
778	4409	4378	4347	4317	4287	4258	4229	4201	4175	4145	4117	4091
780	4420	4389	4358	4328	4298	4269	4240	4211	4185	4155	4128	4101

STANDARDIZATION OF SODIUM THIOSULFATE VERUS POTASSIUM IODATE

1. Weigh, to nearest 0.01 mgm, about 0.065 to 0.070 g of pure potassium iodate (KIO_3), dried at 180°C for 2 hours. Record weight as W. (see Note #1).
2. Transfer to a 250 ml Erlenmeyer flask. Add 2.0 g of potassium iodide (KI) and 50 ml water. Swirl to completely dissolve salts.
3. Add 10 ml of 1:10 Hydrochoric acid (HCl) solution. Solution will turn dark brown from liberated iodine.
4. Titrate immediately with sodium thiosulfate with constant swirling. When the yellow color of the iodine has almost disappeared, add 1 ml 2% starch solution. Continue the titration dropwise to disappearance of the blue color. (Run a blank determination, leaving out the KIO_3).
5. Calculation:

$$\frac{W}{V} \times 28.03608 = N$$

where: W = Weight, in grams, of KIO_3
V = Volume, in ml, of sodium thiosulfate solv.

6. Do in triplicate. Widest difference should be ± 2 ppt.

Note #1 - Instead of weighing three small weighings, about 0.65 to 0.70 grams of KIO_3, weighed to nearest 0.1 mg, may be transferred to a 250 ml volumetric flask. Add water to dissolve salt, then dilute to mark, and mix throughly. Take out 25.0 ml aliquots, by pipet, and transfer to 250 ml Erlenmeyer flasks. Add KI and only 25 ml water and continue above procedure. Use aliquot weight in calculations.

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APPENDIX B

MOLECULAR WEIGHT OF PRODUCT GAS

Run: ____________ Date: ____________

Wt of Bottle + Air ________ ____________ __________

Wt of Bottle ________ ____________ __________

Wt of Air ________ ____________ __________

Wt of Bottle + Gas ________ ____________ __________

Wt of Bottle ________ ________________________

Wt of Gas ________ ____________ __________

Average Wt of Air __________

____

____

__________ ÷ 3 = __________

Average Wt of Gas __________

____

____

__________ ÷ 3 = __________

$$\text{Molecular Wt} = \frac{\text{(average gas wt)}}{\text{(average air wt)}} \times 28.95 = \underline{\hspace{3cm}}$$

APPENDIX C

CONDITIONS USED FOR GAS SOLID CHROMATOGRAPH OF PROCESS GAS SAMPLES

Instrument: Hewlett-Packard Model 700-231 dual column Gas Chromatograph with dual gas sampling valves No. 19020A on each column.

Conditions	Column A	Column B
Column dimensions and packing(s):	4M x 1/4"SS tubing of Linde Molecular Sieve 5A, 60/80 mesh	4M X 1/4" tubing of Waters Associates Porasil A, 100/150 mesh
Gas Sample Loops:	1.0cc	2.0cc
Flow Rate:	60 ml/min.	30 ml/min.
Carrier Gas:	Argon	
Carrier Gas Pressure:	50 psig	
Detector:	Thermal Conductivity with WX Filaments	
Bridge Detector Current:	100 milliamperes	
Temperatures:		
Injection Port	125°C.	
Oven (isothermal)	100°C.	
Detector Block	110°C.	
Chart Speed:	0.5 inches/minute	

Column A: Resolves H_2, O_2, N_2, CH_4, & CO. (Ethane is a later interference).

Column B: Resolves H_2 (air, CH_4, & CO not resolved well), Ethane, CO_2, Propane, Iso- & n-Butanes.

APPENDIX D

AUTOMATICALLY RECORDED POTENTIOMETRIC AQUEOUS AND NONAQUEOUS TITRATION INFORMATION

In this section, the preparation, standardization, general techniques, and use of aqueous and nonaqueous titrants utilizing automatic titration equipment are described in detail. In general, the standardization procedures are the same as for the sample determinations, except that primary standard materials are used. These methods are used to obtain information for relating the distribution of nitrogen in amine or other basic functions to total nitrogen content of solvent and light oil products. In addition phenolic compounds can be similarly related to the oxygen content of such materials.

APPARATUS

See attached "Automatically Recorded Potentiometric Titration Assembly" drawing. (The recorder and syringe pump are set near each other.) Substitution of eqivalent pH meters or recorders to make use of existing equipment is usually practical. The sage pump and an appropriate syringe are not expensive items, and substitution for these items is not recommended. The same equipment is used for all of the potentiometric titrations. Different solvents and titrants are used as described in the specific procedures. Automatic titrators, such as the Sargent Model D titrator or the Precision Dow "Recordomatic" titrator, can be purchased and should function as well as this assembly.

NONAQUEOUS TITRANT SOLUTIONS

General

Working temperatures of the nonaqueous titrant should approximate that of its temperature during standardization;

otherwise the high thermal coefficient of cubic expansion of organic solvents will cause the volume delivered to be in error.

Acetous Perchloric Acid - 0.1 N

To 100 ml glacial acetic acid in a 1000 ml volumetric flask add 9 ml perchloric acid (72%), followed by 20 ml acetic anhydride. Dilute to mark with glacial acetic acid and let stand overnight before standardizing versus THAM. If gels or precipitation occurs when titrating samples, use methanesulfonic acid.

Acetous Methanesulfonic Acid - 0.1 N

To 100 ml glacial acetic acid in a 1000 ml volumetric flask add 6.8 ml of methanesulfonic acid (Eastman Organic Chemicals No. 6320), followed by 2 ml acetic anhydride. Dilute to mark with glacial acetic acid, mix and allow to stand overnight before standardizing versus THAM. (Reference: Caso and Cefola, *Anal. Chim. Acta*. 21, 374-9 (1959))

Tetra n-Butylammonium Hydroxide (TBAH or TBAOH) - 0.1 N

Methanolic 1.OM TBAH (25% in methanol), titration grade, can be obtained from Southwestern Analytical Chemicals, Austin, Texas, Cat. No. 304. (An aqueous 1.OM TBAH solution is also useful in certain cases (SAC Cat. No. 108).) To obtain 0.1 N solutions, 100 ml of the 1.OM solution is diluted to 1000 ml with a desired solvent or solvent mixture. Usually for very weak acids where the alcohol should be kept at a minimum, a 9:1 benzene-methanol solution is obtained by diluting 100 ml of the 1.OM TBAH to 1000 ml with reagent grade benzene. This is the solution usually used for most titrations.

Tetra n-Butylammonium Hydroxide (TBAH or TBAOH) - 0.1 N Continued

Occasionally, other solutions are used for specific problems. All-alcohol solutions are made by diluting the 1.0M TBAH with either methanol, ethanol, isopropanol, etc., for special titrations. Also, a useful solution of 7:2:1 benzene-isopropanol-methanol is made by dissolving 100 ml of 1.0M TBAH in 200 ml of isopropanol, then diluting to 1000 ml with benzene. Do not use old solutions that have absorbed carbon dioxide. (Remarks: TBAH is not soluble in toluene, so do not substitute it for benzene.) Standardize versus benzoic acid.

Alcoholic Potassium Hydroxide - 0.1 N

To 1000 ml of aldehyde-free anhydrous ethanol, add 10 ml of 45% W/W aqueous KOH solution. Standardize versus benzoic acid or potassium acid phthalate. Do not use old solutions that have absorbed carbon dioxide.

Any aldehydes present in the alcohol will interfere by causing the solution to darken and produce a resinous precipitate upon standing. The anhydrous ethanol is purified as follows: Reflux 4 liters of anhydrous ethanol for 3 hours with 30 to 40 g of NaOH or KOH pellets and 25 g of aluminum foil cut into strips and then distill. Collect the first 100 ml of distillate separately for some other use. Distill down to a low pot volume, collecting the distillate in a brown glass bottle. The last portion coming over is collected separately for some other use. (Note: Other alcohols or blends thereof can also be used in special cases.)

AQUEOUS TITRANT SOLUTIONS

Use usual 0.1 or 0.5 N NaOH or H_2SO_4 standard aqueous solutions. Standardize versus potassium acid phthalate or THAM. (Other acids and bases at different strengths versus special standards are also used in special cases.)

STANDARDS

Tris (hydroxylmethyl) aminomethane (THAM), primary standard grade. (This material is also referred to as TRIS, or 2-amino-2-(hydroxymethyl)- 1,3-propanediol.) Obtain from Fisher Scientific Company, No. T-395 or Eastman Organic Chemicals No. 4833).

Dry at 60°C in vacuum oven for 2 hours.

Equivalent Weight 121.14.

Benzoic Acid, primary standard grade. (Matheson, Coleman & Bell, No. CB1008). Dry at 60°C in vacuum oven for 2 hours. Equivalent Weight - 122.12.

Potassium Acid Phthalate (KHP), primary standard grade. (Mallinkrodt No. 6704). Dry at 60°C in vacuum oven for 2 hours. Equivalent Weight - 204.22.

SOLVENTS

All solvents used should be reagent grade. They should be protected from acidic or basic fumes. If a solvent, such as pyridine or DMF, should give a high blank it should be purified before use. Other special titrants, standards, solvents, etc. needed will be discussed in detail in their specific procedures.

GENERAL TITRATION PROCEDURES

(See attached "Automatically Recorded Potentiometric Titration Assembly" drawing.)

Recorder Settings

Set recorder range at 50 mv and chart speed at 1 inch per minute. Other adjustments are as per manufacturer's instructions so that whole span of meter just covers chart span. (Different conditions may be necessary for special cases.)

Meter Settings

Set at 700 mv setting for small inflection points, at 1400 mv setting for large inflection points, or for pH readings if this type of information is desired. Other settings as per manufacturer's or subsequent instructions.

Titration Techniques

Turn on pH meter and recorder and allow to warm up. Remove 50 ml syringe with attached needle from syringe pump. Insert the Teflon needle into required titrant solution and fill syringe by slowly pulling plunger out with a slight rotating motion. After end of plunger has passed the 50 ml mark, invert syringe so that the tip is upward. Slowly push the plunger upward to push all air bubbles out of syringe and needle. Replace syringe in syringe pump holder. Position driving carriage on pump platform to engage mating racks and gears and so the end plate of carriage is next to outer end of syringe plunger. Turn on syringe pump until titrant starts to flow from needle, then turn it off.

Place a 250 ml beaker containing a magnetic stirring bar on the magnetic stirrer. Add ca. 150 ml of specified solvent, using a graduate.

Weigh sample, liquids in suitable hypodermic syringe and solids in weighing scoop, and add to measured solvent in beaker. Some pasty, sticky semi-solid samples may have to be weighed in the beaker directly, then stirring bar and measured solvent added.

Place the rubber stopper containing the electrodes in the beaker. Turn on stirrer and stir to dissolve sample. Insert Teflon needle through glass tube until end is submerged to midway solution. Adjust the pH meter by releasing the "Zero" button and use "Standardization" knob to set meter pointer at desired end of scale.

For acid samples, move pointer to about pH 1 position and for basic samples, move pointer to about pH 13 position. Adjust the recorder so that pen is near the left edge of the chart for acid samples and near the right edge of chart for basic samples. (See attached example standardization curves.) Start the chart drive of the recorder and when the pen is on a major (heavy) line on the chart, simultaneously start the syringe pump. Mark this major line "Start." The recorder will now produce a chart showing the EMF as a function of titrant added. Run the chart until all of the inflection points have been passed; turn off stirrer and pump, and turn recorder to "Stand-by." Remove Teflon needle from beaker, turn pump on for a few seconds to wash out any solution that may have diffused into the titrant in the needle. Remove electrodes and rinse clean with a suitable solvent and store in water.

Inflection Points

The chart will have one or more inflection points which indicate the quantity of titrant required to titrate the components of the sample. The significance of several inflection points is discussed in detail in the specific procedures.

The inflection point of the curve is taken as the end point of the titration. With experience, the inflection point (i.e., change of slope in the middle of the break) is readily found by visual inspection. Count the minutes of time from "Start" of titration to each inflection point. Designate first inflection point time as T_1, second inflection point as T_2, etc. T_1, therefore, represents the time to titrate the first component titrated and T_2-T_1 represents the time to titrate the second component, etc.

Notes

1. With titrations which run several inches of chart length, results are precise and accurate to better than 1% of error. This error can be reduced to a few parts per thousand if the sample size and rate of titrant delivery is properly set.
2. With too small a sample or with trace quantities, precision will suffer. With major and minor quantities it is likely that one precise and one approximate result will often be obtained. This can be corrected by running another sample with appropriate adjustment in sample size if the importance of the result justifies the extra labor.

3. Because of the mechanics of the titration, some reagent must be injected and stirred into the beaker to produce an inflection. In the case where the true result should be zero, the inflection is obviously late. It is possible to differentiate between a nil and a trace by increasing the sample size until a distinctive curve is produced. In non-critical applications, trace or nil curves should be reported nil to the maximum indicated by the inflection observed.

4. The usual titrant delivery rate is about 3 to 4 ml/min.; however in certain cases (e.g., small amount of sample available, low solubility, slow reaction, etc.) it may be necessary to adjust to a slower rate.

STANDARDIZATIONS

Standardization of titrant is done under the same conditions under which the sample determination is to be done. To eliminate any solvent blank influence, the solvent and volume of solvent is kept the same for both standards and samples. (Note: If solvent has a very high blank, it should be pretitrated to a specified indicator color change for both standards and purified samples if possible.)

If the titer of the titrant is determined in the units of milliequivalents per minute (meq/min.), the delivery rate of syringe or true timing of chart speed does not need to be determined; they only need to be constant.

The dried primary standard is weighed and brushed in the titration beaker containing the measured, selected solvent. It is titrated in the method described above, with the titrant to be standardized. The weight of standard should be such as to give at least a 10 to 12 minute titration. Titrant solutions should be restandardized daily, each shift, or when any changes occur.

The titer of a titrant solution is calculated as follows:

$$\frac{W}{T \times E.W.} = \text{Titer in milliequivalents per minute (meq/min.)}$$

where:

W =Weight, in milligrams, of primary standard
T =Time, in minutes, to inflection point
E.W. =Equivalent weight (mg/meq) of primary standard
f =Titer in (milliequivalents/min.) meq/min.

Remarks

There are times and conditions where conventional primary standards do not give comparative standardization results. For this reason, purified samples of the sought component are used as standards. The titer is then calculated as mg of material per minute which is easily calculated as follows:

$$\frac{\text{mg of material}}{\text{Time of inflection point}} = \text{mg/min. titer}$$

Standardization Examples

Tetra-n-butylammonium hydroxide solution is standardized versus benzoic acid. Weigh accurately about 400 to 420 mg of primary benzoic acid and brush into solvent in beaker. Titrate as per general procedure for acid samples. See attached "Standardization Curve of TBAH versus Benzoic Acid." The equivalent weight of benzoic acid is 122.12.

The TBAH solution may also be standardized against standard 0.1000 N sulfuric acid. Accurately pipet 10 ml of standard 0.1 N sulfuric acid into a beaker. Dilute to 150 ml with reagent grade acetone. Titrate as per general procedure for acid samples. Measure distance between the first and second inflection points and determine the titer of the titrant in meq /min.

Perchloric acid solution is standardized versus THAM in acetic acid. Weigh accurately about 380 to 400 mg of primary grade THAM and brush into acetic acid in beaker. Titrate as per general procedure for basic samples. See attached, "Standardization Curve of Acetous Perchloric Acid versus THAM." The equivalent weight of THAM is 121.14.

SELECTED BIBLIOGRAPHY

The literature of non-aqueous titrations has become so enormous in recent years that a complete bibliography is beyond the scope of this discussion. The following textbooks and review articles and the references contained therein should enable the interested reader to pursue further any branch of non-aqueous titration technology.

Textbooks

Fritz, James S., *Acid-Base Titrations in Nonaqueous Solvents*. The G. Frederick Smith Chemical Co., Columbus, Ohio, 1952.

Kucharsky, J. and Safarik, L., *Titrations in Nonaqueous Solvents*. American Elsevier Publishing Co., New York, 1965.

Literature Review Articles

Analytical Chemistry (Reviews), "Acid-Base) Titrations in nonaqueous Solvents."

Riddick, J. A., *24*, 41 (1952); *26*, 77 (1954); *28* 679 (1956); *30*, 793 (1958); *32*, 172R (1960).

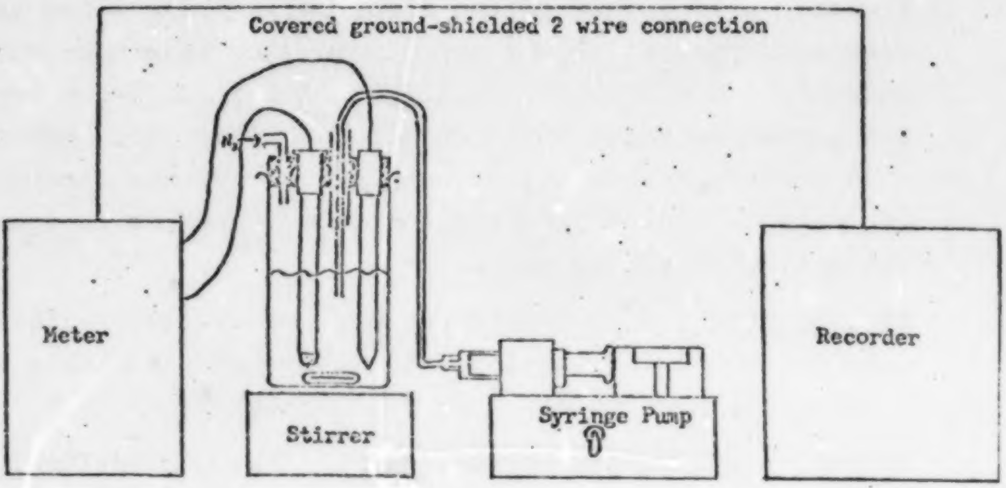
Streuli, C. A., *34*, 302R (1962); *36*, 363R (1964).

Harlow, G. A. and Morman, D. H., *38*, 485R (1966).

"Potentiometric Titrations" are also reviewed in a like manner starting in 1954.

These series of reviews of analytical interests are to be continued every other year.

TITRATION ASSEMBLY



METER, pH-millivolt - Leeds & Northrup, Model 7664 or 7401, or equivalent.

MAGNETIC STIRRER - Magnestir, or equivalent.

MAGNETIC STIRRING BARS - Teflon-coated, 1 7/16" x 3/8", or equivalent.

BEAKERS - 300 ml, tall-form without spout.

RUBBER STOPPER - No. 13 with suitable holes cut for electrodes and glass tubes. Glass tubing is 6mm OD and 4 mm ID, one straight for Teflon needle and a "L" shaped one for nitrogen inlet tube.

GLASS ELECTRODE - Leeds & Northrup #Std. 119-30 or 117163. Store in water, not organic solvent, when not in use. (A platinum electrode may be used here instead).

CALOMEL REFERENCE ELECTRODE - L & N #Std. 119-31. This electrode is modified as follows: Prepare an agar-KNO_3 gel by placing 1.5 gm. of powdered agar in a 100 ml beaker, add 50 ml distilled water, heat on a steam bath with stirring until dissolved. Add 5 gms of potassium nitrate to the beaker and stir until dissolved. Cool the mixture until solidified, and store in a clean capped bottle. Unscrew, remove, and wash the salt bridge tube of the electrode. Place a few small pieces of the gel in the tube, hold with test tube clamp in steam or hot water bath until get is liquidified. Depth of gel should be about 5mm. Cool to solidify gel. Add saturated potassium chloride to tube and screw into electrode as per manufacturer's directions. Store in water, not organic solvent, when not in use.

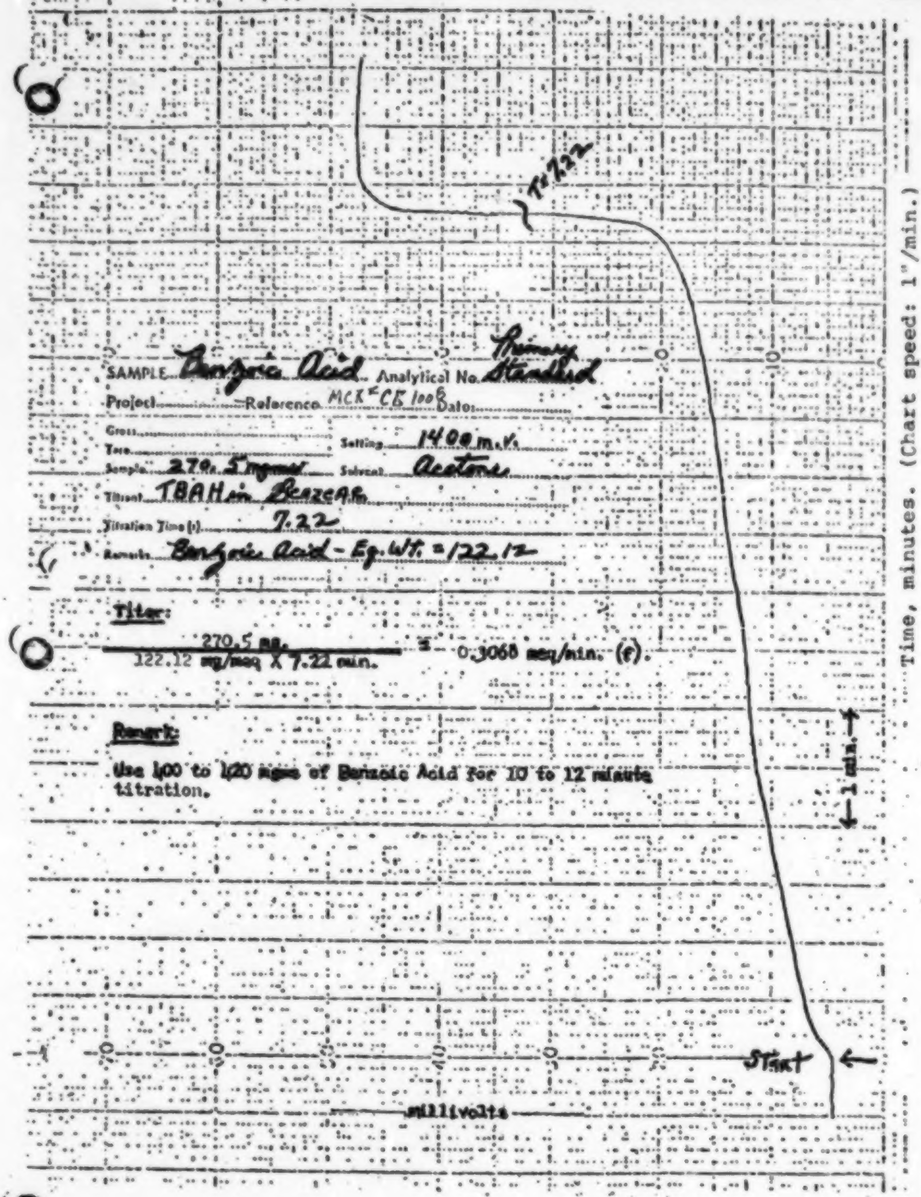
SYRINGE PUMP - Sage Instrument Co., Model 249-2 with alternate gear set Model 259. Using a 50 ml syringe, the rate of delivery is approximately 3 ml per minute.

SYRINGE - Hypodermic. glass, 50 ml. Any conventional brand with lock tip or glass tip and reducer. The "O"-ring type should not be used with organic solvents.

NEEDLE - Teflon tubing 2 ft. long with Kel-F hub. Kontes Glass Co. #K-30818.

RECORDER - E. H. Sargent Co., Model SR or SRL is preferred, however the Heath Built Servo Recorder #EUW-20A with EUA-20-2 motor has been found satisfactory. Chart speed is set at 1 inch per minute by selective drive motor assembly or chart speed control. Recorder is connected to meter by a suitable covered ground-shielded 2 wire cable. Meter, stirrer, syringe pump, and recorder are to be connected to a common ground, such as a water pipe.

Standardization-Curve of Tetra n-Butylammonium Hydroxide (TBAH) vs. Benzoic Acid



SAMPLE Benzoic Acid Analytical No. Primary Standard
Project .... Reference MCK-CE 1008 Date ....
Gross ....
Tare .... Setting 1400 m.v.
Sample 270.5 mgms Solvent Acetone
Titrant TBAH in Benzene
Titration Time (t) 7.22
Remarks Benzoic Acid - Eq. Wt. = 122.12

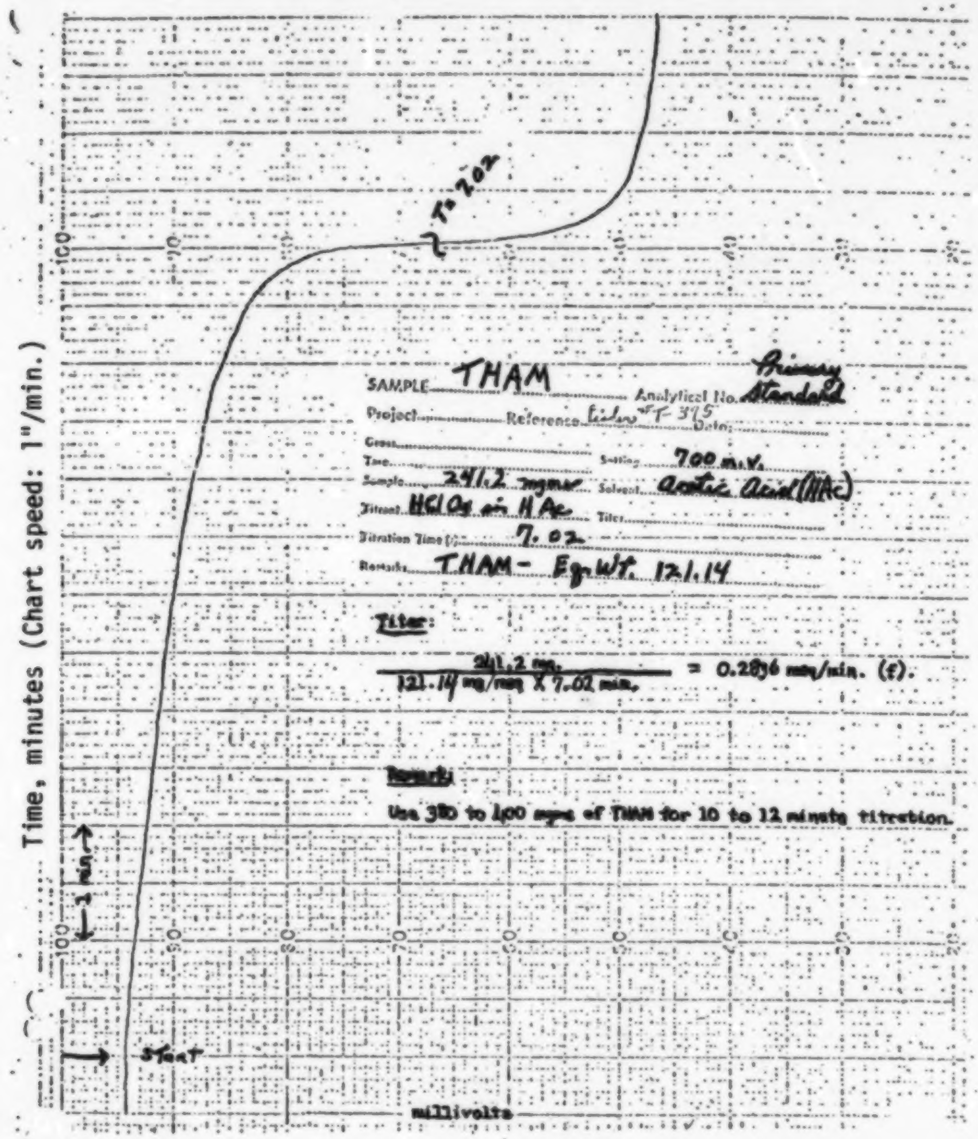
Titer:

$$\frac{270.5 \text{ mg.}}{122.12 \text{ mg/meq} \times 7.22 \text{ min.}} = 0.3068 \text{ meq/min. (f).}$$

Remark:

Use 100 to 120 mgms of Benzoic Acid for 10 to 12 minute titration.

Standardization Curve of Acetous Perchloric Acid vs. Tris (Hydroxymethyl) Aminomethane (THAM)



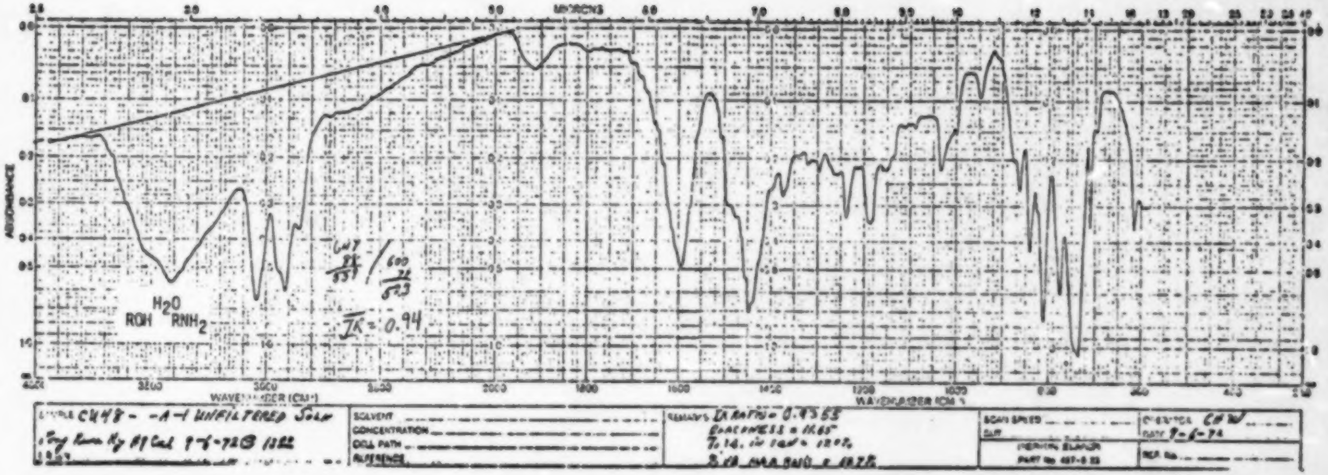
SAMPLE THAM Analytical No. Primary Standard
Project Reference Eiler #T-375 Date
Gross
Tare Setting 700 m.v.
Sample 241.2 mgms Solvent acetic Acid (HAc)
Titrant $HClO_4$ in HAc Titer
Titration Time 7.02
Remarks THAM- Eq. Wt. 121.14

Titer:

$$\frac{241.2 \text{ mg.}}{121.14 \text{ mg/meq} \times 7.02 \text{ min.}} = 0.2836 \text{ meq/min. (f).}$$

Remark:

Use 350 to 400 mgms of THAM for 10 to 12 minute titration.



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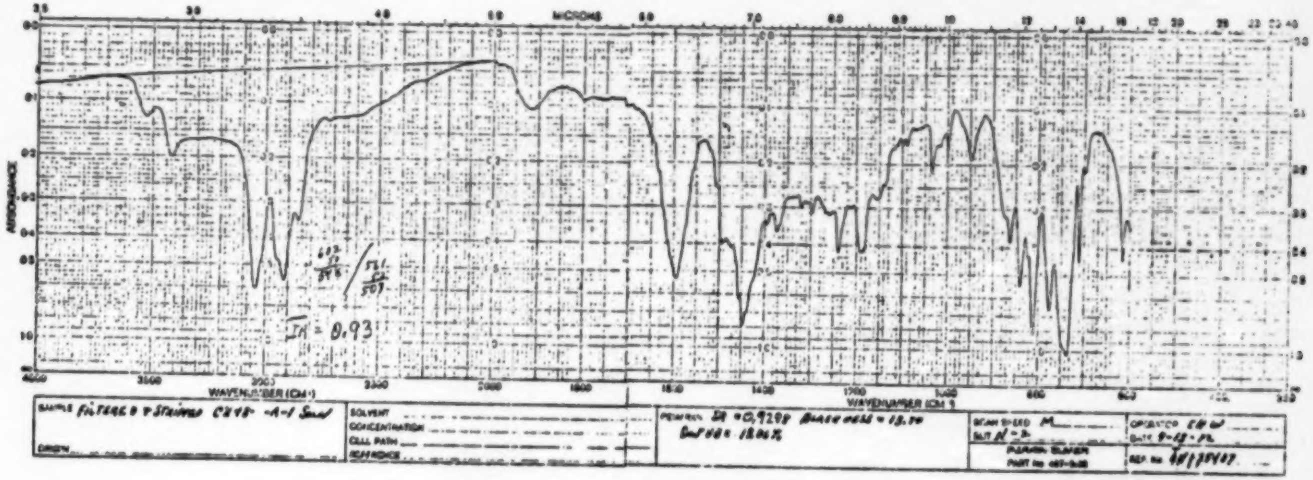
Appendix E IR Spectrum, CU 48A1 Unfiltered Coal Solution



SAMPLE Filtered & Stripped CU48-A-1 Soln

REMARKS IR = 0,9298

SCAN SPEED M

OPERATOR CHW

DATE 9-13-72

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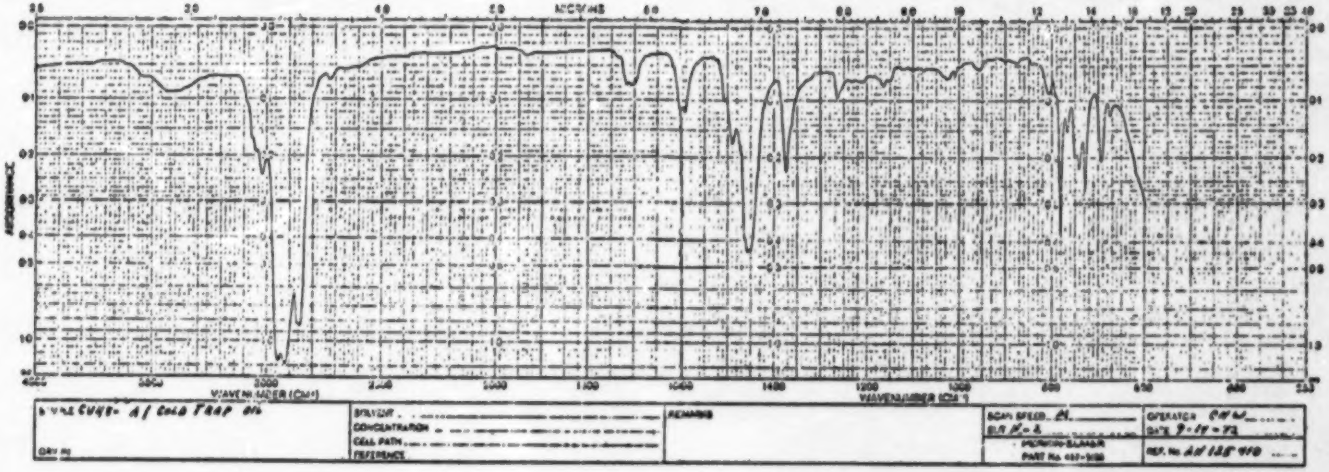
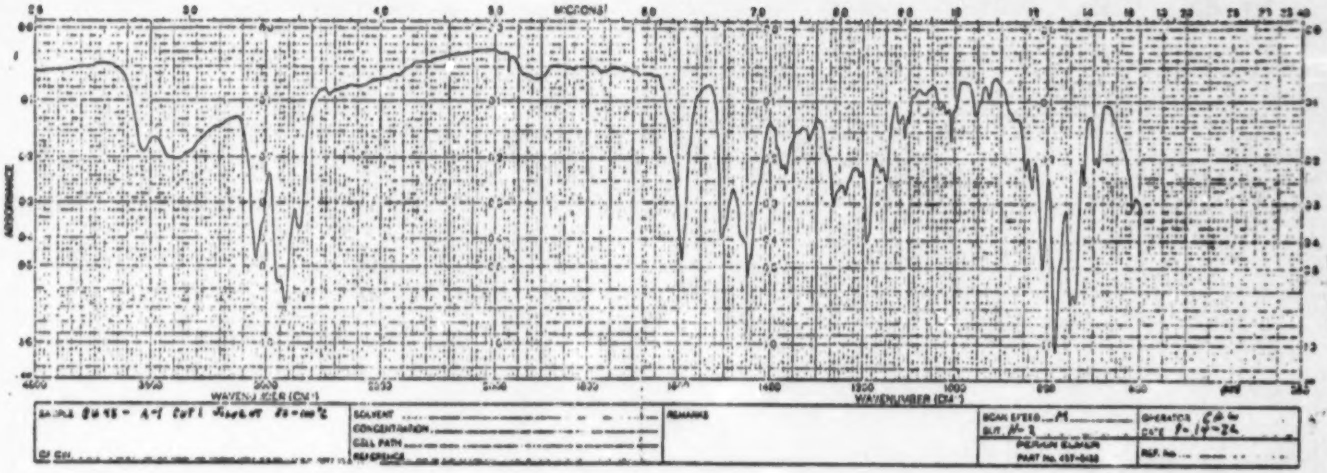
Appendix F IR Spectrum, CU 48A1 Stripped and Filtered Coal Solution



Appendix G IR Spectrum, CU 48A1 Cold Trap Oil



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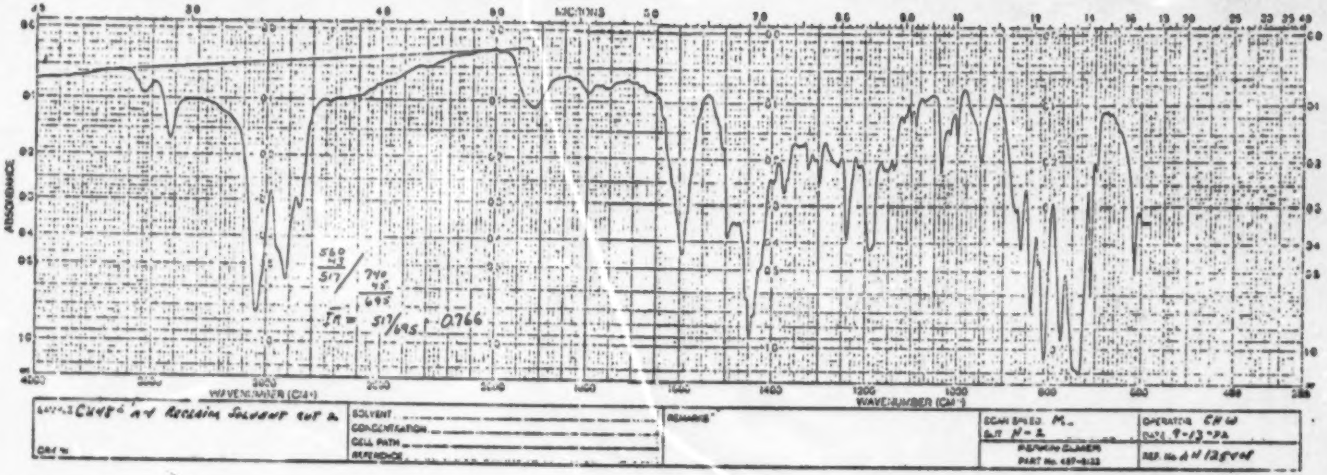
Appendix H IR Spectrum, CU 48A1 Cut 1 011



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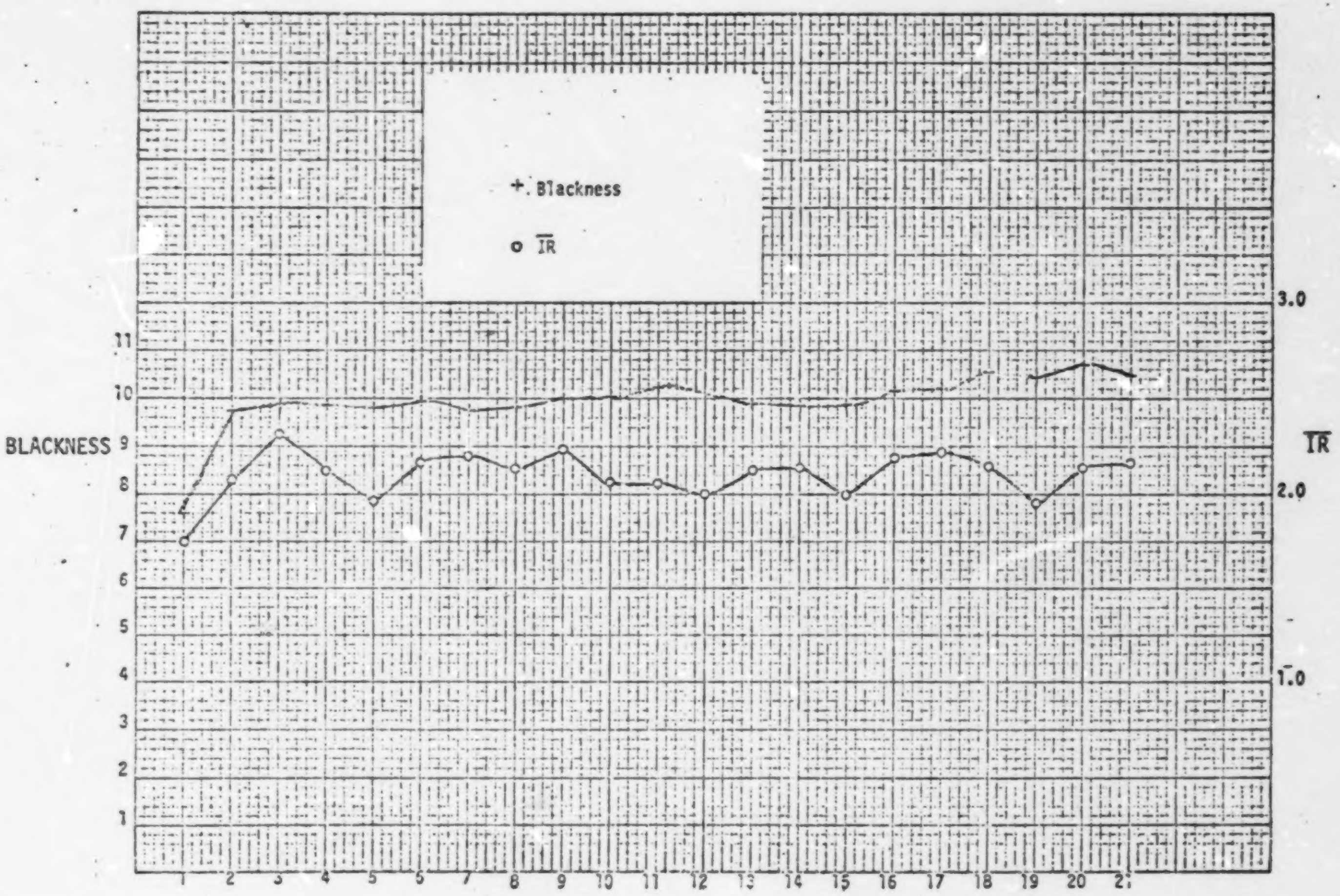
Appendix I IR Spectrum, CU 48A1 Cut 2 011



Appendix J Blackness & $\overline{TR}$ in Successive Samples, CU 80

APPENDIX K
FIRST TRIAL ELEMENTAL BALANCE, CU 48A1

MATERIAL	Wt. GRAMS	% C	% H	% N	% S	% ASH	GRAMS C	GRAMS H	GRAMS N	GRAMS S	GRAMS ASH
INPUT											
Feed Coal	322.3	66.34	4.57	1.29	5.12	16.04	213.8	14.72	4.157	16.501	51.70
Feed Solvent	676.8	90.58	6.04	0.60	0.36		613.0	40.90	4.061	2.436	
Feed Water	20.9		11.19					2.34			
Feed Hydrogen	11.2		100.					11.20			
TOTAL	1031.2						826.8	69.16	8.212	18.937	51.70
OUTPUT - PRIMARY SEPARATION - CORRECTED TO 100% RECOVERY OF FEED											
Gas	37.03	See table 9					15.27	11.83		5.908	
Knock Out Pot	1.1				0.547			0.123		0.006	
Cold Trap H_2O	24.2			0.38	0.821			2.707	0.092	0.199	
Cold Trap Oil	8.0	82.68	12.04	0.212	0.65		5.78	0.843	0.017	0.052	
Filtrate	768.0	90.36	6.25	0.981	0.45		693.96	48.00	7.535	3.456	
Wet Filter Cake	192.9	62.32	3.89	0.895	4.66	27.51	120.21	7.50	1.726	8.989	53.10
TOTAL	1031.2						835.22	71.00	9.370	18.61	53.10
% RECOVERY	100						101	102.6	114	98.3	102.7
OUTPUT - SECONDARY SEPARATION - CORRECTED TO 100% RECOVERY OF FEED											
Gas	37.03	See table 9					15.27	11.83		5.908	
Knock Out Pot	1.1				0.547			0.123		0.006	
Cold Trap H_2O	24.7			0.38	0.821			2.707	0.092	0.199	
Cold Trap Oil	8.0	82.63	12.04	0.212	0.55		5.78	0.843	0.017	0.052	
Cut 1 Oil	29.9	87.47	7.99	0.566	0.20		26.33	2.405	0.169	0.060	
Cut 2 Oil	631.6	91.31	6.02	0.765	0.40		576.53	38.010	4.830	2.526	
Heavy Oil	15.3	85.35	5.15	1.611	0.815		15.19	0.906	0.246	0.125	
Vacuum Bottoms	185.5	87.50	5.23	2.040	0.882	0.179	159.07	9.508	3.782	1.635	0.331
Pyridine Insol.	97.8	33.61	1.67	0.644	8.128	52.88	30.52	1.516	0.632	7.973	51.875
TOTAL	1030.9						828.78	67.90	9.770	18.542	52.206
% RECOVERY	100						100.2	98.2	118.9	97.9	101

APPENDIX L

FIRST TRIAL ELEMENTAL BALANCE, CU 48A2

MATERIAL	Wt. GRAMS	% C	% H	% N	% S	% ASH	GRAMS C	GRAMS H	GRAMS N	GRAMS S	GRAMS ASH
INPUT											
Feed Coal	317.9	66.34	4.57	1.29	5.12	16.04	210.9	14.53	4.100	16.21	50.99
Feed Solvent	667.5	90.58	6.04	0.60	0.36		604.6	40.317	4.005	2.403	
Feed Water	14.6		11.19					1.633			
Feed Hydrogen	11.2		100.					11.2			
TOTAL	1011.2						815.5	67.68	8.105	18.61	50.99
OUTPUT - PRIMARY SEPARATION - CORRECTED TO 100% RECOVERY OF FEED											
Gas	34.23	See table 10					12.136	12.60		5.515	
Knock Out Pot	1.6				1.25			0.176		0.020	
Cold Trap H2O	20.0			0.485	0.841			2.238	0.097	0.168	
Cold Trap Oil	7.0	86.41	11.28	0.219	0.886		6.03	0.789	0.015	0.062	
Filtrate	780.6	89.68	5.94	0.979	0.46		700.0	46.37	7.642	3.590	
Wet.Filter Cake	168.2	59.27	3.54	0.868	(4.772)	30.16	99.60	5.95	1.459	(8.026)	50.73
TOTAL	1011.2						817.87	68.12	9.244	17.40	50.73
% RECOVERY	100						100.3	100.6	114	93.5	99.7
		(Probable Error - Difficult Decomposition of W.F.C. Minerals)									
OUTPUT - SECONDARY SEPARATION - CORRECTED TO 100% RECOVERY OF FEED											
Gas	34.23	See table 10					12.136	12.60		5.515	
Knock Out Pot	1.6				1.25			0.176		0.020	
Cold Trap H2O	20.6			0.485	0.841			2.238	0.099	0.173	
Cold Trap Oil	7.0	86.41	11.28	0.219	0.886		6.05	0.789	0.015	0.062	
Cut 1 Oil	30.1	88.05	7.71	0.560	0.244		26.50	2.321	0.168	0.073	
Cut 2 Oil	627.3	91.73	6.03	0.734	0.377		575.42	37.82	4.603	2.364	
Heavy Oil	17.6	87.26	6.24	1.627	0.842		15.36	1.10	0.286	0.148	
Vacuum Bottoms	181.8	87.32	5.11	1.909	0.944	0.133	158.74	9.289	3.470	1.716	0.24
Pyridine Insol.	90.8	32.02	1.73	0.590	8.930	56.07	29.07	1.57	0.536	8.108	50.91
TOTAL	1011.2						823.3	67.90	9.177	18.179	51.15
% RECOVERY	100						100.9	100.3	113	97.7	100.4